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UPGRADING OF TOTAL ISOMERISATION PROCESSES WITH METAL-ORGANIC FRAMEWORKS

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“Great discoveries and improvements invariably involve the cooperation of many minds”

Alexander Graham Bell

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Abstract

The general goal of this thesis is to develop a novel adsorptive separation process for the octane upgrading of gasoline with considerable potential for commercial application in the petrochemical industry, namely in the separation of pentane and hexane isomers from light naphtha fractions. The production of high-quality gasoline can be approached by efficiently separating these alkane isomers with different degrees of branching. Hence, we endeavoured to perform their discrimination, by adsorption into new types of adsorbents, according to classes of high research octane number (HRON) – isopentane (iC₅; RON 93.5), 2,3-dimethylbutane (23DMB; RON 105) and 2,2-dimethylbutane (22DMB; RON 94) – and low RON (LRON) – n-pentane (nC₅; RON 61.7), n-hexane (nC₆; RON 30), 2-methylpentane (2MP; RON 74.5), and 3-methylpentane (3MP; RON 75.5) – compounds. Therefore, maximising the effectiveness of the conventional Total Isomerisation Process (TIP), that is, to obtain a final isomerate product mixture with a high RON of at least 92, representing a leap forward compared with existing processes.

Different adsorbent materials are evaluated throughout this work, with most of the attention focused on metal-organic frameworks (MOF), which have gained considerable interest in the field of gas adsorption and separation due to their modular synthetic chemistry. To assess the materials separation performance, a new versatile screening apparatus was designed and built to study the adsorption equilibrium and kinetics of single and multicomponent mixtures by measuring fixed bed breakthrough curves with a chromatographic system, fundamental for the scale-up and design of the continuous cyclic adsorption processes. The system is entirely automated, operates over a wide range of working conditions, and allows the real-time analysis of the adsorption column effluent composition. Also, a general mathematical model is developed to qualitatively/quantitatively simulate, analyse and optimise the dynamic behaviour of the experimental fixed bed adsorption system. The numerical package is constructed from fundamental differential equations according to the material and energy conservation laws, taking into account the axial dispersion in the fixed bed and the kinetics of mass transfer (gas to solid) by a simplified linear driving force (LDF) mechanism coupled to convenient adsorption equilibrium models.

We start by evaluating the microporous MOF zeolitic imidazolate framework-8 (ZIF-8), here for the first time with mixtures of both pentane/hexane isomers. The reported data show for all experiments a sorption hierarchy order following the degree of branching: nC₆ > nC₅ >

2MP > 3MP > iC5 $\gg$ 23DMB > 22DMB. The sorption of linear molecules (nC6/nC5) is dominated by thermodynamic equilibrium, with the nC6 reaching loadings at 373 K, twice higher than that of the benchmark zeolite 5A on a mol.kg⁻¹ basis. On the other hand, the sorption of the branched molecules is controlled by kinetic mechanisms due to a steric hindrance, from where the partial separation of mono- (2MP/3MP/iC5) and di-branched (23DMB/22DMB) molecules can be achieved, being the di-branched isomers practically excluded from the material. From the septenary breakthrough experiment at 373 K and total alkane pressure of 50 kPa, a 92 RON ideal productivity of 0.176 mol.dm⁻³ is obtained. The Sips isotherm model conveniently fits the single and multicomponent experimental loadings, and the breakthrough data is suitably predicted by simulations considering strong mass transfer resistances for the branched molecules.

Thereafter, the adsorption of hexane isomers was studied in a series of isorecticular microporous zirconium-carboxylate MOFs, MIL-140 (A, B, and C forms), which are based on different aromatic dicarboxylate linkers. The breakthrough measurements revealed that the MIL-140B form enables their thermodynamic separation by classes nC6 > 2MP/3MP > 23DMB/22DMB with an associated selectivity (LRON/HRON molecules) up to 10 and a 92 RON ideal productivity up to 0.801 mol.dm⁻³ at 343 K. The equilibrium data is also modelled by the Sips isotherm, and the numerical simulations performed with equal mass transfer coefficients for all isomers. Regarding the performances of MIL-140A and MIL-140C, a significant decrease in selectivity (about 2) is evidenced in both cases.

Subsequently, we have shown how a synergistic action of the zeolite 5A and the bioderived aluminium-dicarboxylate MOF MIL-160(Al) give rise to the efficient separation of both pentane and hexane isomers into HRON and LRON fractions. The cooperative approach relies on the unprecedented thermodynamically-driven separation of hexane isomers according to the degree of branching by MIL-160(Al) associated with the steric rejection of all branched molecules by the molecular sieve zeolite 5A. The breakthrough experiment performed with a mixed-bed of shaped adsorbents at a high temperature of 423 K and total alkane pressure of 50 kPa revealed the ideal sorption hierarchy of LRON over HRON alkanes, nC6 > nC5 $\gg$ 2MP > 3MP $\gg$ 23DMB > iC5 $\approx$ 22DMB, together with an outstanding 92 RON ideal productivity of 1.14 mol.dm⁻³. Preliminary cyclic Pressure Swing Adsorption (PSA) experiments indicate the viability of the novel mixed-bed to fractionate these alkane isomers in continuous operation. Langmuir (zeolite) and Dual-site (DSL, MOF) Langmuir isotherms are used to model the equilibrium data and further simulate the breakthrough curves.

The potential application of carbon-based materials for separating pentane and hexane isomers is also addressed in a series of hierarchically structured 3D-printed porous carbons monoliths. Septenary breakthrough experiments are performed in three monoliths with different degrees of CO₂ activation: non-activated and activated at 1133 K for 6 and 12 h, respectively. Results for the non-activated monolith exhibit a separation of n/iso-paraffins through a near molecular sieving mechanism (similar to the effect observed by the zeolite 5A). The branched molecules are practically excluded from the material while the linear ones are adsorbed under some diffusional limitations. This is the first evidence showing that a carbon adsorbent can efficiently separate linear from branched alkanes. The Langmuir isotherm is used to fit the experimental data and for the simulations as well. Regarding the activated monoliths, both show adsorption towards all alkanes with practically no selectivity between them.

Keywords: RON improvement of gasoline;
Pentane and hexane isomers separation by adsorption;
Metal-organic frameworks;
3D-printed carbon monoliths.

Resumo

O objetivo geral desta tese é desenvolver um novo processo de separação por adsorção para aumentar o índice de octano da gasolina com considerável potencial para aplicação comercial na indústria petroquímica, nomeadamente, na separação de isómeros de pentano e hexano a partir de frações de nafta leve. A produção de gasolina de alta qualidade pode ser alcançada pela separação eficiente desses isómeros de alcanos com diferentes graus de ramificação. Por isso, procuramos separá-los, por adsorção em novos tipos de adsorventes, de acordo com as classes de compostos com elevado índice de octano (parafinas HRON) – isopentano (iC₅; RON 93.5), 2,3-dimetilbutano (23DMB; RON 105) e 2,2-dimetilbutano (22DMB; RON 94) - e baixo índice de octano (parafinas LRON) - n-pentano (nC₅; RON 61.7), n-hexano (nC₆; RON 30), 2-metilpentano (2MP; RON 74.5) e 3 -metilpentano (3MP; RON 75.5). Assim, maximizando a eficácia do convencional Processo de Isomerização Total (TIP), que consiste em obter como produto final uma mistura de isómeros com um elevado RON de pelo menos 92, representando um salto em relação aos processos existentes.

Diferentes materiais adsorventes são avaliados ao longo deste trabalho, com maior atenção voltada para as estruturas organo-metálicas (MOF), que ganharam considerável interesse no campo de adsorção e separação de gases devido à sua química sintética modular. Para avaliar a performance de separação dos materiais, um novo e versátil sistema experimental foi projetado e construído para estudar o equilíbrio de adsorção e a cinética de sistemas mono and multicomponentes através de medição de curvas de ruptura em leito fixo com um sistema cromatográfico, fundamental para o dimensionamento de processos contínuos de adsorção cíclica. O sistema é totalmente automatizado, opera em uma ampla gama de condições de trabalho e permite a análise em tempo real da composição do efluente da coluna de adsorção. Além disso, um modelo matemático geral é desenvolvido para simular qualitativamente/quantitativamente, analisar e otimizar o comportamento dinâmico do sistema experimental de adsorção em leito fixo. O pacote numérico é construído a partir de equações diferenciais fundamentais de acordo com as leis de conservação de matéria e energia, levando em consideração a dispersão axial no leito fixo e a cinética de transferência de massa (gás para sólido) por um mecanismo simplificado de força motriz linear (LDF) acoplado a convenientes modelos de equilíbrio de adsorção.

Iniciamos por avaliar a estrutura microporosa do MOF *zeolitic imidazolate framework-8 (ZIF-8)*, pela primeira vez com misturas de ambos os isómeros de pentano/hexano. Os dados

obtidos mostram para todos os experimentos uma ordem de hierarquia de adsorção seguindo o grau de ramificação: $nC6 > nC5 > 2MP > 3MP > iC5 \gg 23DMB > 22DMB$. A adsorção de moléculas lineares ($nC6/nC5$) é dominada por equilíbrio termodinâmico, com o $nC6$ atingindo capacidades à 373 K, duas vezes maiores que a do comercializado atualmente zeólito 5A em base mol.kg^{-1} . Por outro lado, a adsorção das moléculas ramificadas é controlada por mecanismos cinéticos devido a um impedimento estérico, pelo qual a separação parcial das moléculas mono- ($2MP/3MP/iC5$) e bi-ramificadas ($23DMB/22DMB$) pode ser alcançada, sendo os isômeros bi-ramificados praticamente excluídos do material. A partir da experiência de curva de ruptura com uma mistura setenária à 373 K e pressão total de alcano de 50 kPa, uma produtividade ideal igual a $0.176 \text{ mol.dm}^{-3}$ é obtida para um RON de 92. O modelo de Sips se ajusta convenientemente às capacidades de adsorção dos sistemas mono e multicomponentes, e as curvas de ruptura são adequadamente reproduzidas pelas simulações considerando fortes resistências à transferência de massa para as moléculas ramificadas.

Posteriormente, a adsorção de isômeros de hexano foi estudada na isorreticular série de estruturas microporosas de zircônio-carboxilato MOFs, MIL-140 (formas A, B e C), que são baseados em diferentes ligantes dicarboxilatos aromáticos. As medições das curvas de ruptura revelaram que a forma MIL-140B permite a separação termodinâmica dos isômeros por classes $nC6 > 2MP/3MP > 23DMB/22DMB$ com uma seletividade associada (moléculas LRON/HRON) de até 10 e uma produtividade ideal de até $0.801 \text{ mol.dm}^{-3}$ à 343 K para um RON de 92. Os dados de equilíbrio também são modelados pela isoterma de Sips, e as simulações numéricas realizadas com coeficientes de transferência de massa iguais para todos os isômeros. Em relação aos desempenhos do MIL-140A e MIL-140C, uma diminuição significativa na seletividade (cerca de 2) é evidenciada em ambos os casos.

Subsequentemente, é mostrado como uma ação sinérgica do zeólito 5A e do bioderivado alumínio-dicarboxilato MOF MIL-160(Al) dá origem a uma separação eficiente dos isômeros de pentano e hexano em frações de HRON e LRON. A abordagem cooperativa baseia-se na separação termodinâmica dos isômeros de hexano de acordo com o grau de ramificação pelo MIL-160(Al), associado à rejeição estérica das moléculas ramificadas pela peneira molecular do zeólito 5A. O experimento de curva de ruptura realizado com um leito misto de adsorventes na alta temperatura de 423 K e pressão total de alcano de 50 kPa revelou a hierarquia ideal de adsorção de LRON sobre HRON alcanos, $nC6 > nC5 \gg 2MP > 3MP \gg 23DMB > iC5 \approx 22DMB$, juntamente com uma excelente produtividade ideal de 1.14 mol.dm^{-3} para um RON de 92. Experimentos cíclicos preliminares de adsorção por modulação de pressão (PSA)

indicam a viabilidade do novo leito misto para fracionar esses isômeros de alcano em operação contínua. As isotermas de Langmuir (zeólito) e Dual-site Langmuir (DSL, MOF) são usadas para modelar os dados de equilíbrio e simular as curvas de ruptura experimentais.

A potencial aplicação de materiais à base de carbono para separar os isômeros de pentano e hexano também é abordada em uma série de monólitos porosos de carbonos hierarquicamente estruturados impressos em 3D. Experimentos de curva de ruptura com misturas setenárias são realizados em três monólitos com diferentes graus de ativação de CO₂: não ativado e ativado à 1133 K por 6 e 12 h, respectivamente. Os resultados para o monólito não ativado exibem a separação de n/iso-parafinas através de um mecanismo próximo ao peneiramento molecular (semelhante ao efeito observado pelo zeólito 5A). As moléculas ramificadas são praticamente excluídas do material enquanto as moléculas lineares são adsorvidas sob algumas limitações de difusão. Esta é a primeira evidência a mostrar que um adsorvente de carbono pode separar eficientemente alcanos lineares de ramificados. A isoterma de Langmuir é usada para ajustar os dados experimentais e também para as simulações. Em relação aos monólitos ativados, ambos adsorvem todos os alcanos e praticamente não há seletividade entre eles.

Palavras-chave: Aumento do RON da gasolina;
Separação de isômeros de pentane e hexano por adsorção;
Estruturas organo-metálicas;
Monólitos de carbono impressos em 3D.

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List of symbols

Nomenclature

a_{ac}	specific area of the adsorption column, (m^{-1})
a_s	specific area of the adsorbent, (m^{-1})
b_i	adsorption affinity constant of component i , (kPa^{-1})
$b_{i,\infty}$	adsorption affinity constant of component i at infinite temperature, (kPa^{-1})
c_{pg}	heat capacity of the gas mixture, ($\text{J.mol}^{-1}.\text{K}^{-1}$)
$\hat{c}_{pg}$	specific heat capacity of the gas mixture ($\text{J.kg}^{-1}.\text{K}^{-1}$)
$c_{p,i}$	heat capacity of component i in the gas mixture, ($\text{J.mol}^{-1}.\text{K}^{-1}$)
$\hat{c}_{p,i}$	specific heat capacity of component i in the gas mixture, ($\text{J.kg}^{-1}.\text{K}^{-1}$)
c_{ps}	heat capacity of the adsorbent, ($\text{J.kg}^{-1}.\text{K}^{-1}$)
C_f	concentration of the adsorbate species in the feed, (mol.m^{-3})
C_T	total concentration of the gas mixture, (mol.m^{-3})
$C_{T,f}$	total concentration of the gas mixture in the feed, (mol.m^{-3})
d_s	diameter of the adsorbent, (m)
D_{ax}	axial mass dispersion coefficient, ($\text{m}^2.\text{s}^{-1}$)
D_i	diffusivity constant of component i , ($\text{m}^2.\text{s}^{-1}$)
D_{ij}	binary diffusivity for the pair of components i and j , ($\text{m}^2.\text{s}^{-1}$)
D_m	molecular diffusion coefficient, ($\text{m}^2.\text{s}^{-1}$)
$D_{m,i}$	molecular diffusion coefficient of component i , ($\text{m}^2.\text{s}^{-1}$)
ΔE_i	activation energy for diffusion of component i , (J.mol^{-1})
F_f	molar flow rate of adsorbate species in the feed, (mol.s^{-1})
F_i	molar flow rate of component i , (mol.s^{-1})
F_T	total molar flux of the gas mixture, ($\text{mol.m}^2.\text{s}^{-1}$)
$F_{T,f}$	total molar flux of the gas mixture in the feed, ($\text{mol.m}^2.\text{s}^{-1}$)
h_f	film heat transfer coefficient (gas-adsorbent), ($\text{W.m}^{-2}.\text{K}^{-1}$)
h_w	internal convective heat transfer coefficient (gas-column wall), ($\text{W.m}^{-2}.\text{K}^{-1}$)
H_i	Henry's constant of component i , ($\text{mol.kg}^{-1}.\text{kPa}^{-1}$)
ΔH_i	heat of adsorption of component i , (J.mol^{-1})

k_e^0	axial thermal conductivity in the stagnant bed, (W.m ⁻¹ .K ⁻¹)
k_g	thermal conductivity of the gas mixture, (W.m ⁻¹ .K ⁻¹)
$k_{g,i}$	thermal conductivity of component i in the gas mixture, (W.m ⁻¹ .K ⁻¹)
$k_{LDF,i}$	mass transfer coefficient of component i , (s ⁻¹)
$k_{LDF\infty,i}$	mass transfer coefficient of component i at infinite temperature, (s ⁻¹)
k_s	thermal conductivity of the adsorbent, (W.m ⁻¹ .K ⁻¹)
K_{ax}	axial heat dispersion coefficient, (W.m ⁻¹ .K ⁻¹)
L	length of the adsorption column, (m)
m_s	mass of adsorbent, (kg)
M_i, M_j	Molar mass of component i and j , respectively, (kg.mol ⁻¹)
M_m	average molar mass of the gas mixture, (kg.mol ⁻¹)
n_i	heterogeneity index of component i , (-)
$n_{i,0}$	heterogeneity index of component i at reference temperature, (-)
N	number of data points (experimental loadings)
N_c	number of components in the gas mixture, (-)
N_M	number of adsorbent materials packed in the adsorption column, (-)
N_u	Nusselt number, (-)
p_i	partial pressure of component i in the gas mixture, (kPa)
p_T	total alkane pressure, (kPa)
Pe_h	heat Peclet number, (-)
Pr	Prandtl number, (-)
P_s	ideal adsorbent productivity at a 92 RON, (mol.dm ⁻³)
P_T	total pressure of the gas mixture in the adsorption column, (kPa)
q_{exp}	loading of adsorbate species (experimental), (mol.kg ⁻¹)
q_i	loading of component i (given by the isotherm model = q_{model}), (mol.kg ⁻¹)
$\bar{q}_i$	averaged loading of component i , (mol.kg ⁻¹)
q_{mix}	total mixture loading (experimental), (mol.kg ⁻¹)
$q_{sat,i}$	saturation loading capacity of component i , (mol.kg ⁻¹)
$q_{sat,i,0}$	saturation loading capacity of component i at reference temperature, (mol.kg ⁻¹)
Q	isosteric heat of adsorption, (J.mol ⁻¹)

$\bar{\Delta}q$	mean relative deviation between experimental loading and isotherm model, (-)
r	crystallite radius of the adsorbent, (m)
R	universal gas constant, (J.mol ⁻¹ .K ⁻¹)
R_{ac}	internal radius of the adsorption column, (m)
Re	Reynolds number, (-)
R_s	radius of adsorbent particles, (m)
S	adsorption selectivity, (-)
S_{BET}	specific surface area by BET theory, (m ² .g ⁻¹)
$S_{Langmuir}$	specific surface area by Langmuir theory, (m ² .g ⁻¹)
S_{QSDF}	specific surface area by QSDF theory, (m ² .g ⁻¹)
t	time, (s)
t_{rt}	mean retention time, (s)
t_{RON92}	time interval for recovering a 92 RON product, (s)
t_s	saturation time, (s)
T^*	dimensionless temperature in the diffusion collision integral, (-)
T_g	temperature of the bulk gas phase, (K)
$T_{g,f}$	temperature of the gas mixture in the feed, (K)
T_s	temperature of the adsorbent particles, (K)
$T_{s,0}$	reference temperature of the adsorbent, (K)
T_w	temperature of the adsorption column wall, (K)
v_{sup}	superficial velocity of the gas mixture, (m.s ⁻¹)
v_{int}	interstitial velocity of the gas mixture, (m.s ⁻¹)
V_{ac}	volume of the adsorption column, (m ³)
y_i	molar fraction of component i in the gas mixture, (-)
$y_{i,f}$	molar fraction of component i in the gas mixture in the feed, (-)
z	distance along the length of the adsorption column (axial coordinate), (m)

Greek Letters

α_i	constant parameter of component i (heterogeneity index - Sips isotherm), (-)
γ_1, γ_2	constants for the bed tortuosity and turbulent mixing, respectively, (-)

δ_i	thermal expansion factor of component i , (-)
ε_b	porosity of the packed bed (void fraction), (-)
$\varepsilon_i, \varepsilon_j$	maximum energy of attraction for the components i or j , respectively, (J)
ε_{ij}	maximum energy of attraction for the pair of components i and j , (J)
θ	fractional coverage, (-)
κ	Boltzmann constant, (J.K ⁻¹)
μ_g	viscosity of the gas mixture, (Pa.s)
μ_i, μ_j	viscosity of component i and j in the gas mixture, respectively, (Pa.s)
ρ_a	apparent density of the adsorbent, (Eq. 3.4: kg.dm ⁻³ or Eq. 3.25: kg.m ⁻³)
ρ_b	bulk density, (kg.m ⁻³)
ρ_{b_mb}	bulk density of the mixed-bed, (kg.m ⁻³)
ρ_g	density of the gas mixture composition, (kg.m ⁻³)
σ_i, σ_j	collision diameter for the components i and j , respectively, (Å)
$\sigma_{i,j}$	collision diameter for the pair of components i and j , (Å)
τ	residence time of the gas mixture in the fixed bed, (s)
Φ_{ij}	dimensionless quantity for viscosity and thermal conductivity for the pair of components i and j , (-)
$\Omega_{D_{ij}}$	collision integral for diffusion for the pair of components i and j , (-)

Subscripts

ac	adsorption column
avg	average
ax	axial
c	component
exp	experimental
f	feed (or film h_f)
g	gas
h	heat
i, j	i or j component (or adsorbent material x_j)
int	interstitial
m	mass

<i>mb</i>	mixed-bed
<i>mix</i>	mixture
<i>o</i>	reference condition
<i>s</i>	solid (adsorbent particle)
<i>sup</i>	superficial
<i>sat</i>	saturation
<i>T</i>	total
<i>w</i>	wall
∞	infinite condition

Acronyms and Abbreviations

abtc	3,3',5,5'-azobenzene-tetracarboxylate
AC	adsorption column
APC	advanced pneumatic control
BAPO	phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide
BDP ²⁻	1,4-benzenedipyrazole
BET	Brunauer-Emmett-Teller
BF	bubble flowmeter
BPSD	barrel per stream day
bptc	3,3',5,5'-biphenyltetracarboxylate
ca.	approximately, from Latin “ <i>circa</i> ”
CAD	computer-aided design
CAU	Christian-Albrechts-Universität
CBMC	configurational-bias Monte Carlo
CC	capillary column
ClbIm	5-chlorobenzimidazole
CoRE	computational ready experimental
CSS	cyclic steady state
dabco	1,4-diazabicyclo[2,2,2]octane
DiaMM	diamondoid microporous material

DLP	digital light processing
DMF	N,N-dimethylformamide
DOctP	bis(2-ethylhexyl) phthalate
dpt	2,4-di(4-pyridinyl)-1,3,5-triazine
DSL	dual-site Langmuir
DVB	divinylbenzene
e.g.	for example, from Latin “ <i>exempli gratia</i> ”
ENS	École Normale Supérieure
ESA	electrical swing adsorption
FD	finite differences
FDCA	2,5-furandicarboxylic acid
FEP	fluorinated ethylene propylene
FID	flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
fum	fumarate
GC	gas chromatograph
HClbIm	5-chlorobenzimidazole
Hdmtrz	3,5-dimethyl-1H,1,2,4-triazole
HMF	5-(hydroxymethyl)furan-2-carbaldehyde
H ₂ BDC	1,4-benzenedicarboxylic acid
H ₂ FTZB	2-fluoro-4-(1H-tetrazol-5-yl)benzoate
H ₂ NDC	2,6-naphthalenedicarboxylic acid
H ₂ BPDC	biphenyl-4,4'-dicarboxylic acid
H ₂ tba	4-(1H-tetrazol-5-yl)-benzoic acid
H ₃ bttotb	4,4',4''-(benzene-1,3,5-triyltris(oxy))tribenzoic acid
HO	heating oven
HRON	high research octane number
ICE	internal combustion engine
iC5	iso-pentane (2-methylbutane)
i.e.	that is, from Latin “ <i>id est</i> ”

IFP	Institut Français du Pétrole
Im	imidazolate
IMAP	Institut des Matériaux Poreux de Paris
IUPAC	International Union of Pure and Applied Chemistry
KRICT	Korea Research Institute of Chemical Technology
LDF	linear driving force
LRC	loading ratio correlation
LSR	light straight-run naphtha
LRON	low research octane number
LTA	Linde Type A
MeIm	2-methylimidazolate
MFC	mass flow controller
MIL	material of Institute Lavoisier
MIP	mercury intrusion porosimetry
MOF	metal-organic framework
MON	motor octane number
nC5	n-pentane
nC6	n-hexane
nIm	2-nitroimidazole
NPM	noncovalent microporous material
ON	octane number
PC	personal computer
PD	purge displacement
PDE	partial differential equation
PETA	pentaerythritol tetraacrylate
PSA	pressure swing adsorption
PT	pressure transducer
PXRD	powder x-ray diffraction
QSDFT	quenched solid density functional theory
RON	research octane number

RVP	Reid vapor pressure
SBU	secondary building unit
S/SP	split/spitless
SEM	scanning electron microscopy
SLA	stereographically
SOD	sodalite
SP	syringe pump
STL	standard tessellation language
TCD	thermal conductivity detector
tcpb	1,2,4,5-tetrakis(4-carboxyphenyl)-benzene
TGA	thermogravimetric analysis
TIP	total isomerization process
TL	transfer line
tpa	tonnes per annum
TR	temperature regulator
TSA	temperature swing adsorption
UiO	University of Oslo
UOP	Universal Oil Products
VP	vacuum pump
ZIF	zeolite imidazolate framework
1,4-NDC	1,4-naphthalenedicarboxylate
22DMB	2,2-dimethylbutane
23DMB	2,3-dimethylbutane
2MP	2-methylpentane
3MP	3-methylpentane
4,4'Bipy	4,4'-bipyridine
6FDCA	2,2-bis(4-carboxyphenyl)-hexafluoropropane

1 INTRODUCTION

This introductory chapter aims to emphasise the relevance and motivation of the work developed during this PhD thesis. It provides the current status of manufacturing automotive gasoline in the modern petroleum refinery, accompanying the importance of the light naphtha isomerisation processes and consequent separation of alkane isomers by the degree of branching in the pentane and hexane range. In this context, the gasoline production by the Total Isomerisation Process (TIP) technology is highlighted with the associated challenge that needs to be overcome to maximise its overall effectiveness by producing a final isomerate product with at least an average RON of 92 in the post-reactor separation/recycling paraffins adsorption unit. Based on that, the objectives for the PhD work are established for the study and modelling of the adsorption of pentane and hexane isomers in new adsorbents, given the improvement of conventional TIP processes.

1.1 Relevance and Motivation

The development of the crude oil refining industry and the internal combustion engine (ICE) have influenced each other since the beginning of the 20th century.¹ Both petroleum refineries and the automobile industry are constantly challenged to continually improve their products to meet increasingly severe governmental energy efficiency and emission standards. For example, in producing an appropriate fuel for use in an ICE, the petroleum industry blends a plurality of hydrocarbon-containing streams to obtain a product that will meet the governmental combustion emission regulations and the engine manufacturers' performance fuel criteria.^{1,2} Similarly, engine manufacturers usually design spark ignition type internal combustion engines around the stringent specifications of the fuel, attempting to inhibit the auto-ignition (or detonation) phenomenon to the maximum extent, which typically results in knocking and, potentially, engine damage.³ This synergistic action naturally requires a compromise between fuel properties and engine design.

In the case of gasoline, the preferred automobile fuel, the combustion quality is evaluated by the octane number (ON), which measures the fuel's resistance to auto-ignition. The higher this resistance is, the higher the fuel's efficiency to produce work, and the combustion proceeds as a smooth explosion instead of a self-ignite and rapid inefficient detonation.¹⁻³ The ON is often referred to as the antiknock characteristic of gasoline and can be measured at low engine speeds (research octane number – RON)⁴ or high engine speeds (motor octane number – MON).⁵ The most common octane rating worldwide shown on the pumps at filling stations is the RON (in North America, it is often shown the arithmetic average of RON and MON). According to the European motor fuel specifications (Euro 5 – DIR 98/70), gasoline should have at least a RON equal to 95 for its use in modern automotive combustion engines.¹

Gasoline fuel characteristics have a significant influence on vehicle emissions and fuel consumption. Now that reducing harmful emissions is a matter of global concern, stringent regulations affecting gasoline composition have been enacted in most regions of the world to mitigate the detrimental impacts on the environment and human health caused by its combustion.⁶ These regulations include many clean fuel initiatives such as lead phase-out, minimisation of volatility (Reid vapor pressure - RVP), limits on sulphur, benzene, aromatics, and olefin content, and addition of oxygenates.¹ Unfortunately, aromatics and olefins are high-octane molecules, so reducing their concentration in gasoline causes a decrease in the RON and, consequently, fuel quality. Therefore, researchers in academia and industry have focused

their attention on petroleum refining to improve the current processes in view of increasing the concentrations of high-octane hydrocarbons in their gasoline to provide maximum quality, meeting at the same time the stringent challenge of clean-fuel regulations while maintaining the economic viability of the entire process.

The global oil demand roared back as the world began to recover from the coronavirus pandemic. According to Statista, the need for gasoline in 2020 was around 23.8 million barrels daily, which is forecast to climb to 27.7 by 2030.⁷ Although vehicles using different energies such as electric and fuel cell vehicles have recently attracted much attention and have entered a period of rapid development, there is still a consensus that the ICE will continue to be the primary power device for the foreseeable future.^{8,9}

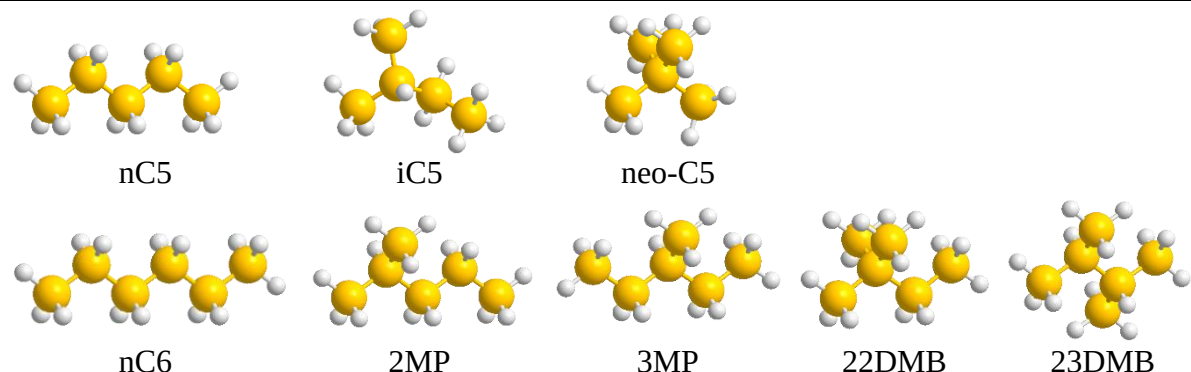
1.1.1 The Role of Paraffins Isomerisation

Automotive gasoline is one of the most highly refined products leaving the modern petroleum refinery. Typically, it is a blend of the products from different refinery streams, including isomerate (paraffinic), reformat (aromatic), hydrocracked (paraffinic and aromatic), polymer (olefinic or paraffinic), alkylate (paraffinic), and fluid catalytic cracked (olefinic and aromatic) fractions, which results in a complex mixture that essentially contains all classes of hydrocarbons in the C₄ to C₁₂ range.^{1,2} The relative concentrations of the different hydrocarbons vary considerably depending on the source of crude oil, refinery process, and product specifications. Moreover, the gasoline is manufactured to meet the property fuels specifications and regulations, not to achieve a specific distribution of these hydrocarbons by class and size.

A number of investigations on the RON number of individual hydrocarbons have brought to light some general rules. For example, straight-chain alkanes (normal paraffins) have the least desirable knocking characteristics, and this becomes progressively worse as the molecular weight increases. Branched-chain alkanes (iso-paraffins) have higher RON numbers than the corresponding normal isomers, which increases as the degree of branching of the chain is increased. Olefins have noticeably higher RONs than the related paraffins, and the aromatics usually have relatively high RON numbers.² Based on that, the worldwide introduction of stringent regulations demanding clean fuels (limiting the content of benzene, aromatics, and olefins) has caused many refiners to adjust the gasoline composition to a greater extent of iso-paraffins. In this context, the role of alkane isomerisation is inevitable as the RON number of alkanes usually increases with the degree of branching.

The isomerisation of light straight-run (LSR) naphtha plays a key role in meeting octane demand in the gasoline pool. The LSR stream is about 90% paraffinic (mostly pentane and hexane normal alkanes), clear of sulphur and aromatics, and has a very low benzene content. In addition, it is characterised by a low octane number, with the average RON ranging between 60 – 70.¹⁰ The main objective of isomerisation is to maximise the RON values of the linear alkanes by rearranging their molecular structures into their more valuable mono- or multi-branched isomers. Table 1.1 shows the RON values for pentane and hexane isomers. Iso-pentane (iC5; 93.5) has a RON value of nearly 30 numbers higher than n-pentane (nC5; 61.7). Similarly, the di-branched hexanes 2,2-dimethylbutane (22DMB; 94) and 2,3-dimethylbutane (23DMB; 105) show values at least 64 numbers higher than n-hexane (nC6; 30). The mono-branched hexanes 2-methylpentane (2MP; 74.5) and 3-methylpentane (3MP; 75.5) isomers have similar RON, whose values are about 40 numbers higher than nC6.

Table 1.1 | Physicochemical properties of pentane and hexane isomers.

Molecular structure*							
							
Alkane		Molecular dimensions (nm) ¹¹			Kinetic diameter (nm) ¹²	Boiling point (K) ¹⁰	RON ¹³
chemical name	symbol	length	height	width			
n-pentane	nC5	0.93	0.48	0.42	0.43	309	61.7
iso-pentane	iC5	0.80	0.64	0.55	0.50	301	93.5
neo-pentane*	neoC5	0.67	0.55	0.67	0.62	283	98.0
n-hexane	nC6	1.06	0.48	0.42	0.43	342	30.0
2-methylpentane	2MP	0.93	0.64	0.55	0.50	333	74.5
3-methylpentane	3MP	0.93	0.62	0.55	0.50	339	75.5
2,2-dimethylbutane	22DMB	0.80	0.56	0.67	0.62	323	94.0
2,3-dimethylbutane	23DMB	0.80	0.69	0.55	0.56	331	105.0

* Yellow spheres are carbon atoms and grey spheres are hydrogen atoms.

* neoC5, a di-branched isomer of nC5, is not generated under isomerization conditions.¹⁰

Ideally, the isomerisation would convert all the feed paraffins into the most desired highest RON branched structures: nC5 to iC5, and nC6 to 22DMB and 23DMB. However, the catalytic reaction is incomplete due to the limitations of thermodynamic equilibrium, and the isomerised product consists of unreacted linear alkanes and its mono- and di-branched isomers. The alkane isomers distribution mainly depends on the type of catalyst employed, where the most common are platinum dispersed on chlorinated alumina (Pt/Al₂O₃-Cl), sulphated zirconia (Pt/SO₄-ZrO₂), and zeolites (Pt/zeolite) as shown in Figure 1.1.^{14,15} The more active the catalyst, the lower the reaction temperature range. Typically estimated yields revealed that around 15 - 25 wt.% of unconverted linear alkanes and about 20 - 25 wt.% of mono-branched hexanes are still present in the isomerate product stream. Concerning the slight benzene amount, all the feed is saturated to cyclohexane, which, in turn, is partially converted into nC6.¹⁰ Based on its chemistry, the isomerisation process represents one of the most economic pathways available for reducing the benzene content in gasoline. Currently, about 2.5 million barrels of pentanes and hexanes are processed daily.¹

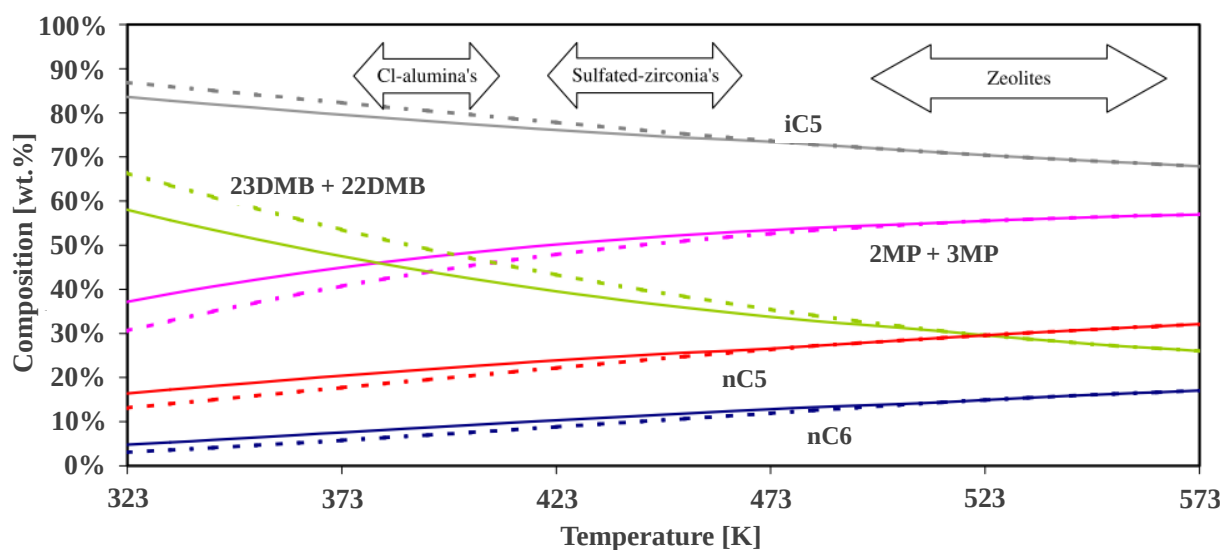


Figure 1.1 | Thermodynamic equilibrium distribution of pentane and hexane isomers as a function of temperature. The solid line represents the liquid phase and the dashed line gas phase equilibrium. Adapted from the ref. 14

After the catalytic conversion, the octane rating of the light naphtha generally shows an increase by about 10 to 12 RON. To obtain a better RON of the pentane/hexane cut, the industry strives to separate the isomerate product into high octane and low octane fractions. The efficient separation of alkane isomers with different degrees of branching, however, remains a critical yet challenging process in the petrochemical industry of today.¹⁶ Conventional heat-driven

distillations, the primary separation technique currently used in industry, can accomplish this task; but it comes with huge capital investment and high energy consumption. The similar boiling points of these paraffins (Table 1.1) means that a repeated evaporating-condensing cycle of the isomerate mixture, associated with high reflux ratios and reboiling rates, should be performed to achieve the separation of compounds having considerably different RON values (such as mono- and di-branched hexanes). Add to this, a large number of distillation trays are required (≥ 60), resulting in a very tall column.^{17,18} Generally, the energy consumed in most distillations is at least one and frequently two orders of magnitude greater than the minimum thermodynamic work of separation.¹⁹

Alternatively, material-assisted separation technology, such as adsorptive separation by porous solids, which makes use of the difference in molecular dimensions/shape of the molecules, is employed as a supplementary technology for alkane isomer separation. Aside from lowering the energy cost substantially, adsorptive separation through porous media is environmentally beneficial as it significantly reduces carbon dioxide emissions.¹⁶ Having the ability to completely separate linear alkanes from their respective branched isomers via size exclusion over its pore aperture, zeolite 5A (Ca-LTA - Linde Type A) is the current benchmark sorbent in practice.¹⁰ The material consists of AlO_4 and SiO_4 tetrahedrons joined together by shared oxygen atoms. It exhibits a cubic structure with eight sodalite cages centred at the corners, which are connected by four-membered rings forming a three-dimensional (3D) network (Figure 1.2). This arrangement creates a large cage of about 1.14 nm in diameter, accessible by eight-membered ring windows with a free aperture near 0.5 nm that behaves as a molecular sieve, allowing only the adsorption of linear alkanes while excluding any nonnormal hydrocarbons.²⁰ It, therefore, enables the efficient removal of the unconverted linear alkanes from the isomerate mixture.

The major application using zeolite 5A molecular sieve for the gas phase separation of isomerate fractions is the TIP process, among the first and most successful adsorption processes applied in industry.²¹ This patented system assigned to Universal Oil Products (UOP) integrates the Once-Through Zeolitic Isomerisation process (formerly known as the Shell Hysomer process) with the IsoSiv adsorption separation technology.¹⁰ The complete removal of the linear alkanes on the adsorption unit generates a branched isomerate product stream with an average RON ranging between 87 – 90, which is used for gasoline blending.¹⁰ The adsorbed linear alkanes are recycled back to the catalytic reactor to undergo additional isomerisation reactions (Figure 1.3a).

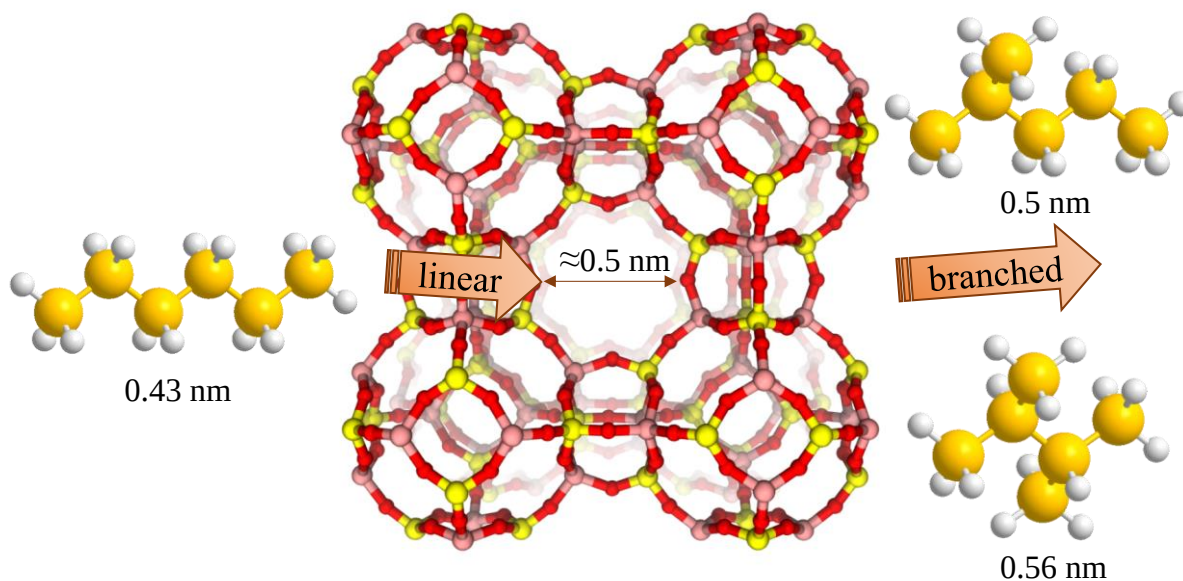


Figure 1.2 | Schematic view of zeolite 5A and the molecular sieving effect for n/iso-paraffins.

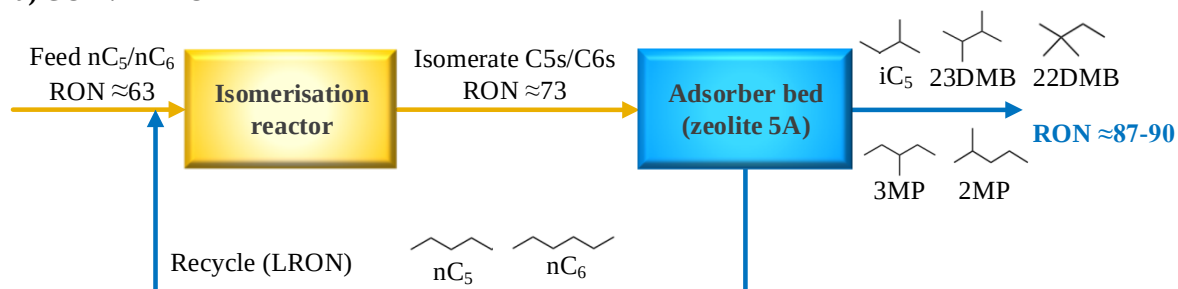
1.2 Objectives and Layout

This thesis aims to contribute for the development of a new adsorptive separation process with considerable potential for commercial application in the refining industry, namely, in the separation of high RON (HRON > 90) paraffins from light naphtha fractions through the TIP process. Since mono- and di-branched alkanes are excluded from the pores of zeolite 5A, their discrimination is not possible, and the presence of the low RON (LRON < 90) mono-branched hexanes 2MP and 3MP in the final isomerate stream limits its overall performance. It should be noted that the increase of 1 unit of the RON corresponds to about a cost of US\$ 900,000 per year for a 300,000 tpa (tonnes per annum) hydro-isomerisation unit.²²

Axens (a commercial branch of Institut Français du Pétrole – IFP) attempted to improve the conventional TIP process by coupling a deisohexanizer column to the adsorption unit for recycling the 2MP and 3MP back to the isomerisation reactor. As a result, an increased methylpentane conversion into dimethylbutane is obtained, thus raising the RON of the final product. The so-called Hexorb process provides isomerate having over 90 RON (typically 91 – 92 RON). However, this advanced hybrid technology requires a high capital investment of US\$ 22 million for an 8000 BPSD (barrel per stream day) unit,²³ besides substantially increasing the operating costs due to the heavy energy fractionation column. One alternative path to make a leap forward in this field would be to find an optimal single adsorbent or a synergy effect of mixed-bed adsorbents with excellent pentane and hexane isomer separation performance for a

complete fractionation of the TIP reactor effluent into HRON (iC₅/22DMB/23DMB) and LRON (nC₅/nC₆/2MP/3MP) fractions (Figure 1.3b). Searching for novel materials is challenging for this end.

a) CONVENTIONAL



b) UPGRADED

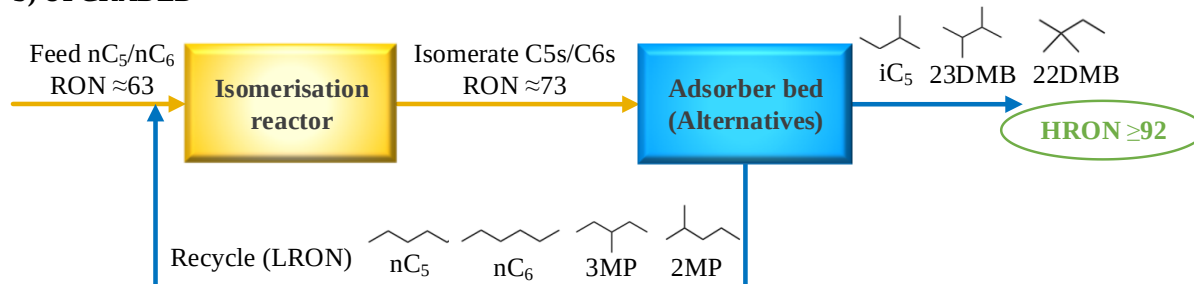


Figure 1.3 | Schematic representation of the TIP process: a) Conventional and b) Upgraded.

To date, extensive effort has been primarily deployed to assess the separation performance of other zeolites with different pore sizes and shapes.^{24–34} For example, it has been demonstrated previously that zeolite BETA partially discriminate mono and di-branched hexane isomers via a thermodynamically-controlled separation mechanism.³⁴ Also, pure silicalite form was shown to enable a kinetically-driven separation of branched hexanes owing to the slow diffusion of the di-branched molecule in its pore structure.³⁰ However, so far, none of the existing zeolites has reached optimum performance to meet the industrial needs of separating complex pentane and hexane feeds. That is why TIP processes remain unchanged in terms of their performance from the late 70's, with the basic separation of n/iso-paraffins by adsorption in a post-reactor adsorption unit filled with the molecular sieve zeolite 5A.

Zeolites are robust and thermostable materials due to their inorganic-based structures, which capacitate them for the usually harsh industrial conditions.³⁵ However, they lack porosity tenability, and the insufficiency in precise control of pore structure of these materials limits their separation efficiency for challenging gas separation, especially for fractionating gas

molecules with a high degree of similarity in physical/chemical properties.³⁶ Therefore, advanced materials showing a pore structure of high modulating accuracy are needed for such an ambitious target. In this context, the newest class of porous materials, the metal-organic frameworks (MOFs), which integrate the merits of tuneable pore size, shape, and chemistry, have provided the promise to address this and many other growing industrial separations demands. Motivated by that, different MOFs are analysed throughout this thesis with the aim of discovering materials able to better separate branched alkanes, being this class of porous media the main focus of this work.

The flowchart in Figure 1.4 describes the main steps to be followed for developing an adsorptive separation process. It requires a comprehensive understanding of the equilibrium and kinetics of adsorption and their impact on the dynamics of fixed bed adsorption column, which is fundamental for the design of continuous cyclic operations either from Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA) or simply Purge Displacement (PD). Accurate knowledge of such behaviour can be obtained by combining experimental data (from single and multicomponent breakthrough experimental systems) with computational techniques (mathematical modelling). The ultimate stage leads to the scale-up at the industrial level, in which pilot tests (optimised cyclic operation) with an adsorber bed at the kilogram scale should be performed. Finally, it is important to highlight that the associated cost of the best process performance plays a decisive role before decision for its further commercialisation.

This thesis comprises eight chapters: the present one highlighting the significance of the work; one reporting the current knowledge about the studied matter (state of the art); one describing the fundamental tools used to evaluate/screening new adsorbent materials for the separation of pentane and hexane isomers; four chapters dealing with the detailed description of results from data collected on three different kind of MOFs and one in a 3D-printed carbon-based monolith; and to finish, one showing the concluding remarks. Figure 1.5 illustrates the contents of the work in a flow diagram with a brief description below.

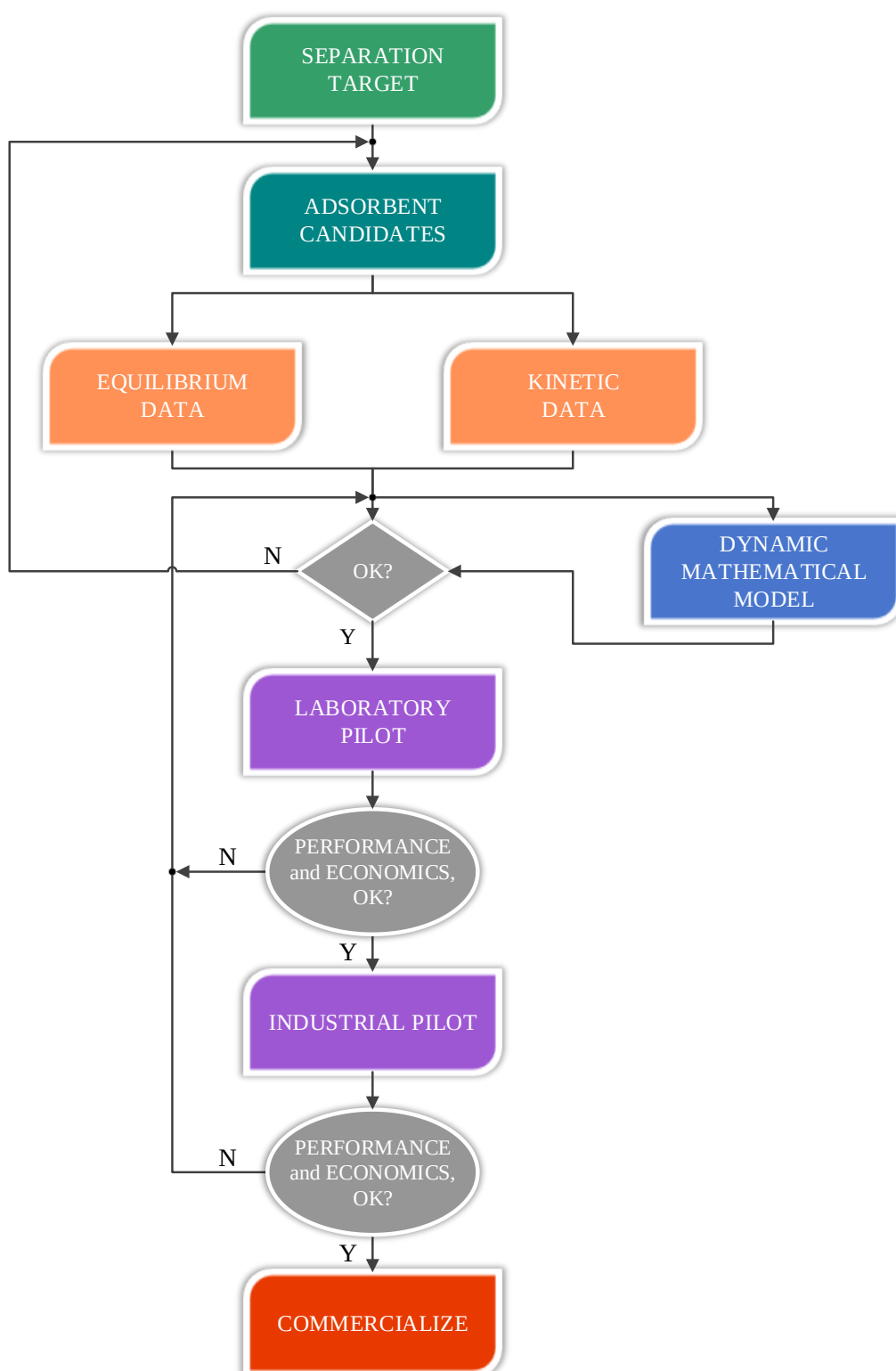


Figure 1.4 | Flow diagram to develop an adsorptive separation process. Adapted from the ref. 37

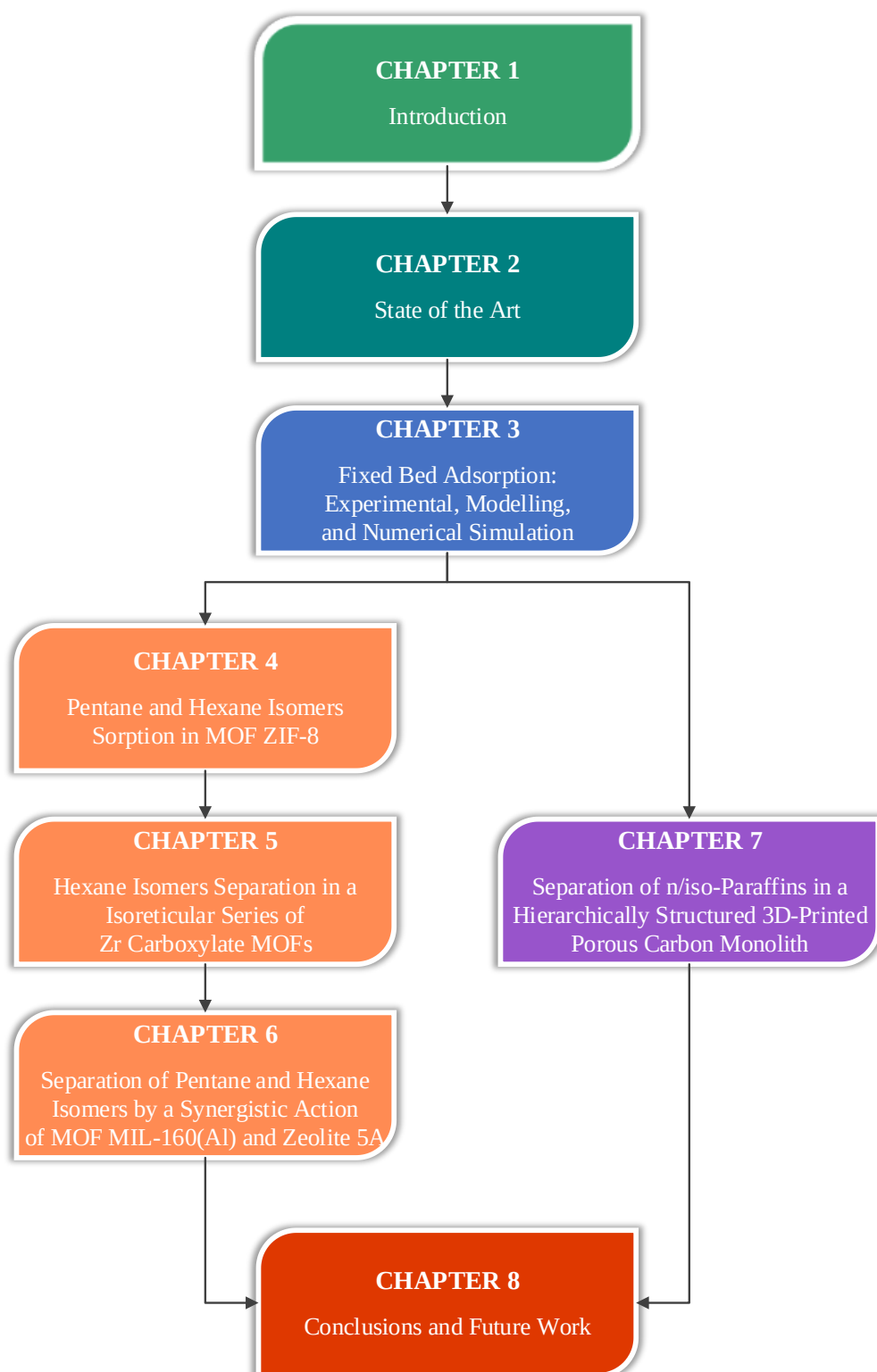


Figure 1.5 | Flow diagram representation of the thesis organisation.

Chapter 2 presents a state of the art review of the main progress in using MOFs for the adsorptive separation of pentane and hexane isomers. Significant breakthroughs in the field, from early exploratory efforts to recent studies on the design of tailored materials, are underlined and classified according to different adsorption mechanisms. The challenges that still need to be addressed are also identified.

Chapter 3 gathers the methodology adopted to study new adsorbent materials for separating pentane and hexane isomers. First, it is introduced the new fixed bed adsorption unit developed. Thereafter, the procedure to analyse the dynamics of single and multicomponent experiments through the measurement of breakthrough curves is highlighted, which results in collecting adsorption equilibrium data with further modelling. Finally, a general fixed bed mathematical model is deduced to simulate the experimental observations to get insight into the sorption mechanisms and respective optimisation of working conditions.

Chapter 4 describes the systematic study of the adsorption behaviour of pentane and hexane alkane isomers in MOF ZIF-8. An extensive series of breakthrough experiments addressing single (linear pentane and hexane) and multicomponent (hexane and hexane/heptane isomers) systems are performed to shed light on the influence of different working conditions on their separation. Temperature, alkane pressure, and residence time of the gas in the bed are analysed, demonstrating that their careful selection can lead to a complete separation of linear from branched paraffins and a partial separation of mono- and di-branched alkanes.

Chapter 5 deals with the adsorption of hexane isomers in a series of isorecticular Zr carboxylate MOFs (forms A, B, and C), with focus given to MIL-140B form. Single and multicomponent experiments are performed at different temperatures and alkane pressures in this material, which showed a thermodynamic separation of the isomers according to the degree of branching, i.e., linear > mono-branched > di-branched isomers. Additional multicomponent experiments in MIL-140A and C are carried out at a fixed temperature to evaluate the impact of the pore size in the series.

Chapter 6 shows the study performed in MOF MIL-160(Al) through the measurement of single and multicomponent breakthrough curves of pentane and hexane isomers under different working conditions, that leads to the development of a novel adsorptive process for the efficient separation of the isomers into valuable HRON and LRON fractions. The innovative technology comprises a mixed-bed adsorber strategy relying on two different adsorption mechanisms: the thermodynamic separation of hexane isomers by classes in MIL-160(Al) and the selective size-exclusion of branched alkanes by the molecular sieve zeolite 5A.

Chapter 7 demonstrates through multicomponent experiments the efficient separation of n/iso-paraffins of pentane and hexane isomers in a hierarchically structured 3D-printed porous carbon monolith, similar to the one observed a long time ago in the molecular sieve zeolite 5A. Although this thesis mainly focuses on MOFs, this chapter was included because it represents the first work dealing with monolithic adsorbents for separating linear from branched alkane isomers. It provides an important reference for the utilisation of structured materials in this field of separation, besides opening a new frontier for carbon-based materials.

Chapter 8 summarises the main conclusions of this thesis. Further research directions are also presented.

1.3 References

- (1) Treese, S. A.; Pujadó, P. R.; Jones, D. S. J. *Handbook of Petroleum Processing*, 2nd Ed.; Springer, 2015.
- (2) Speight, J. G. *The Chemistry and Technology of Petroleum*, 5th Ed.; CRC Press, 2014.
- (3) Wang, Z.; Liu, H.; Reitz, R. D. Knocking Combustion in Spark-Ignition Engines. *Prog. Energy Combust. Sci.* **2017**, 61, 78–112.
- (4) ASTM International. *ASTM D2699-19e1 - Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel*; 2019.
- (5) ASTM International. *ASTM D2700-19e1 - Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel*; 2019.
- (6) Bolden, A. L.; Kwiatkowski, C. F.; Colborn, T. New Look at BTEX: Are Ambient Levels a Problem? *Environ. Sci. Technol.* **2015**, 49, 5261–5276.
- (7) Statista®. Demand outlook for selected oil products worldwide from 2020 to 2045 <https://www.statista.com/statistics/282774/global-product-demand-outlook-worldwide/> (accessed Jun 1, 2022).
- (8) Kalghatgi, G. Is It Really the End of Internal Combustion Engines and Petroleum in Transport? *Appl. Energy* **2018**, 225, 965–974.
- (9) Reitz, R. D.; Ogawa, H.; Payri, R.; Fansler, T.; Kokjohn, S.; Moriyoshi, Y.; Agarwal, A.

- K.; Arcoumanis, D.; Assanis, D.; Bae, C.; Boulouchos, K.; Canakci, M.; Curran, S.; Denbratt, I.; Gavaises, M.; Guenther, M.; Hasse, C.; Huang, Z.; Ishiyama, T.; Johansson, B.; Johnson, T. V.; Kalghatgi, G.; Koike, M.; Kong, S. C.; Leipertz, A.; Miles, P.; Novella, R.; Onorati, A.; Richter, M.; Shuai, S.; Siebers, D.; Su, W.; Trujillo, M.; Uchida, N.; Vaglieco, B. M.; Wagner, R. M.; Zhao, H. IJER Editorial: The Future of the Internal Combustion Engine. *Int. J. Engine Res.* **2020**, *21*, 3–10.
- (10) Meyers, R. A. *Handbook of Petroleum Refining Processes*, 3rd Ed.; McGraw-Hill Education, 2004.
- (11) Jiménez-Cruz, F.; Laredo, G. C. Molecular Size Evaluation of Linear and Branched Paraffins from the Gasoline Pool by DFT Quantum Chemical Calculations. *Fuel* **2004**, *83*, 2183–2188.
- (12) Wang, H.; Li, J. Microporous Metal-Organic Frameworks for Adsorptive Separation of C5-C6 Alkane Isomers. *Acc. Chem. Res.* **2019**, *52*, 1968–1978.
- (13) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels. *Science*. **2013**, *340*, 960–964.
- (14) Vermeiren, W.; Gilson, J. P. Impact of Zeolites on the Petroleum and Petrochemical Industry. *Top. Catal.* **2009**, *52*, 1131–1161.
- (15) Aitani, A.; Akhtar, M. N.; Al-Khattaf, S.; Jin, Y.; Koseoglo, O.; Klein, M. T. Catalytic Upgrading of Light Naphtha to Gasoline Blending Components: A Mini Review. *Energy and Fuels* **2019**, *33*, 3828–3843.
- (16) Sholl, D. S.; Lively, R. P. Seven Chemical Separations to Change the World. *Nature* **2016**, *532*, 435–437.
- (17) Larry W. Kruse. Fractionation for a C6 Paraffin Isomerization Process. US 4,831,209, 1989.
- (18) Lynn H. Rice. Fractionation of Paraffin Isomerization Process Effluent. US 6,573,417 B1, 2003.
- (19) Whyte, T. E.; Yon, C. M.; Wagner, E. H. *Industrial Gas Separations*; American Chemical Society, 1983.

- (20) Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A. *J. Am. Chem. Soc.* **1956**, *78*, 5963–5971.
- (21) Holcombe, T. C. Total Isomerization Process. US 4,210,771, 1980.
- (22) Guisnet, M.; Gilson, J. *Zeolites for Cleaner Technologies*; Imperial College Press, 2002; Vol. 3.
- (23) Domergue, B.; Watripont, L. Paraffins Isomerisation Options. *Pet. Technol. Q.* **2005**, Q2, 21–25.
- (24) Huddersman, K.; Klimczyk, M. Separation of Branched Hexane Isomers Using Zeolite Molecular Sieves. *AIChE J.* **1996**, *42*, 405–408.
- (25) Huddersman, K.; Klimczyk, M. Separation of Hexane Isomers on Zeolites Mordenite and Beta. *J. Chem. Soc. - Faraday Trans.* **1996**, *92*, 143–147.
- (26) Luna-Triguero, A.; Gómez-Álvarez, P.; Calero, S. Adsorptive Process Design for the Separation of Hexane Isomers Using Zeolites. *Phys. Chem. Chem. Phys.* **2017**, *19*, 5037–5042.
- (27) Denayer, J. F.; Souverijns, W.; Jacobs, P. A.; Martens, J. A.; Baron, G. V. High-Temperature Low-Pressure Adsorption of Branched C5-C8 Alkanes on Zeolite Beta, ZSM-5, ZSM-22, Zeolite Y, and Mordenite. *J. Phys. Chem. B* **1998**, *102*, 4588–4597.
- (28) Dandekar, H. W.; Funk, G. A.; Zinnen, H. A. Process for Separating and Recovering Multimethyl-Branched Alkanes. US 6,069,289, 2000.
- (29) Calero, S.; Smit, B.; Krishna, R. Separation of Linear, Mono-Methyl and Di-Methyl Alkanes in the 5-7 Carbon Atom Range by Exploiting Configurational Entropy Effects during Sorption on Silicalite-1. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4390–4398.
- (30) Jolimaitre, E.; Ragil, K.; Tayakout-Fayolle, M.; Jallut, C. Separation of Mono- and Dibranched Hydrocarbons on Silicalite. *AIChE J.* **2002**, *48*, 1927–1937.
- (31) Maeson, T.; Harris, T. Process for Producing High RON Gasoline Using ATS Zeolite. US 7,029,572 B2, 2006.
- (32) Maesen, T.; Harris, T. Process for Producing High Ron Gasoline Using CFI Zeolite. US

- 7,037,422 B2, 2006.
- (33) Krishna, R.; van Baten, J. M. Screening of Zeolite Adsorbents for Separation of Hexane Isomers: A Molecular Simulation Study. *Sep. Purif. Technol.* **2007**, *55*, 246–255.
 - (34) Bárcia, P. da S. Separation of Light Naphtha for the Octane Upgrading of Gasoline: Adsorption and Membrane Technologies and New Adsorbents. Ph.D. Thesis, Faculty of Engineering of the University of Porto, 2010.
 - (35) Valencia, S.; Rey, F. *New Developments in Adsorption/Separation of Small Molecules by Zeolites*; Springer, Cham, 2020; Vol. 184.
 - (36) Lin, R. B.; Xiang, S.; Zhou, W.; Chen, B. Microporous Metal-Organic Framework Materials for Gas Separation. *Chem* **2020**, *6*, 337–363.
 - (37) Adsorption Research Inc. Adsorption Research, Development & Evaluation <https://www.adsorption.com/evaluation-research-and-development/>.

2 STATE OF THE ART

This chapter comprehensively reviews the main progress and achievements in using MOFs for the adsorptive separation of pentane and hexane isomers over the past decades. Significant breakthroughs in the field, from early exploratory efforts to the latest advancements in designing tailored materials by different approaches, such as topologically directed design and the mixed-ligand strategy, are highlighted. Based on possible separation mechanisms governing the adsorption behaviour - thermodynamic equilibrium coming from host-guest interactions, kinetic effect, or molecular sieving - selective adsorptions in MOFs are classified, and primary relationships between adsorption properties and framework features are systematically discussed. Moreover, this chapter also summarises specific challenges that must be considered when evaluating MOF materials for the targeted separation and possible future directions.

2.1 Introduction

The past two decades have witnessed explosive growth in the research and development of materials known as MOFs.¹ These novel materials are constructed by joining inorganic metal-containing units (also known as secondary building units - SBUs) with organic linkers, using strong bonds (reticular synthesis/chemistry) to create well-defined open crystalline frameworks with permanent porosity.^{2,3} Generally, the organic units are ditopic or polytopic carboxylates (and other similar negatively charged molecules).⁴ Compared to the classical adsorbents such as zeolite silicates and carbon-based materials, MOFs are endowed with some unique advantageous structural features that offer great opportunities for revolutionising industrial applications, especially in gas storage and separation:

- 1) Modular designability: the reticular chemistry of MOFs enables the prospective design of target materials with accurate structural predictability, allowing the fine control of framework topology and pore characteristics to make “materials on demand”.^{2,4,5} Different from porous zeolite mainly constructed by SiO₄ tetrahedra linking through O²⁻/OH⁻, the flexibility with which the metal SBUs and organic linkers can be combined leads MOFs to exhibit a diverse platform of pore structures of uniform sizes, such as spherical, cylindrical, slit, tubular pores interconnecting and/or isolating on a 1-dimensional (1D), 2D, or 3D direction;^{4,6-9}
- 2) Structural and functional tunability: pores/channels size within MOFs can be systematically tuned at the molecular level by using organic linkers of different lengths to coordinate respectively with metal ions without changing the underlying topology of the prototypal structure, which potentially improve their sieving effects for the selective separation of gas molecules.¹⁰⁻¹⁵ Moreover, it is further possible to modulate the surface chemistry by readily immobilising functional sites (open metal sites, Lewis basic or acidic sites, polar amino or hydroxyl groups, etc.) onto the internal surface of MOFs to induce specific interactions for the recognition of gas molecules during the equilibrium process and, thus remarkably enhancing their gas storage and separation capacities;¹⁶⁻²⁵
- 3) High porosity and surface area: MOFs are endowed with a characteristic porosity of greater than 50% of its crystal volume, and the surface area values typically range from 1000 to 10000 m².g⁻¹, which can aid with adsorption site accessibility and give rise to a significant separation working capacity;⁴

4) Structural flexibility: in some cases, MOFs possess dynamic, “soft” structures that respond to external stimuli, such as pressure, temperature, and guest molecules. This sensitivity to external stimuli enables MOFs to exhibit specific properties such as pressure/temperature-dependent size/shape exclusion or a gate-opening effect, therefore improving their separation performances.^{26–34}

These remarkable features rendered MOFs the most promising candidates for the separation challenges of the industrially valuable hydrocarbons, as a number of strategies can be employed to rationally design near-ideal adsorbents following reticular chemistry principles. Indeed, using MOFs as adsorbents, significant advancements have been made in the separation of methane/acetylene, acetylene/ethylene, ethane/ethene, ethane/ethylene, propane/propene, propane/propylene, C₄ compounds, benzene/cyclohexane, aromatic C₈ isomers, styrene/ethylbenzene, and halogenated aromatics.^{35–44} The separation of pentane and hexane isomers aiming for gasoline upgrading has also attracted a great deal of attention. The continuously devoted effort has produced considerable achievements, which will be explored in this state of the art.

2.2 MOFs for Pentane and Hexane Isomer Separation

Numerous research evaluating MOF materials for pentane and hexane isomer separation has been reported focusing on experimental techniques (Table A1, *Appendix A*) and/or computational simulations. The most representative breakthrough progressions (Figure 2.1) in the field are presented in this chapter, from early examples to recent studies on the rational design of tailored materials. A deep understanding of structure-property relationships between MOFs and adsorbates is discussed in detail to provide a comprehensive insight into the underlying adsorption separation mechanisms.

Based on the pore size and shape of the adsorbent and/or the binding affinity from adsorption sites, the adsorptive separation of gaseous mixtures can be performed by discriminating adsorbate molecular sizes, shapes, polarities, polarizabilities, packing abilities, etc. Therefore, generally speaking, separation based on different mechanisms can be roughly categorised as thermodynamic equilibrium separation, kinetic separation, and molecular sieving (steric) separation or combinations thereof.^{45–47}

Thermodynamic equilibrium separations usually happen on adsorbents whose pore apertures are large enough to accommodate all adsorptive species without noticeable strong diffusional limitations. The separation performance is governed by the differences between the relative binding affinities of the adsorptive species and adsorbent surface (host-guest interactions). The interaction strength is dictated by the properties of the targeted guest molecules and the surface characteristics of the adsorbent, which can be enhanced by pore surface modification with strong binding sites. Kinetic separation originates from the differences in diffusion rates of adsorptive species into the pore channel of the adsorbent. Guest molecules with substantially higher mobilities will occupy the pore spaces firstly, resulting in separation before the adsorption equilibrium of the slower guest molecules. Such differences in diffusion rates can be exploited in transient fixed bed separation methods (dynamic system) by controlling the exposure time. Molecular sieving separation arises from the shape/size exclusion. It is driven by the incompatibility between the kinetic diameter of the adsorptive species and the pore size dimensions, which allows only small and properly shaped adsorptive species to diffuse while completely excluding the bulkiest ones, therefore allowing the attainment of infinite selectivity.^{45–47} Hence, it is generally considered as the ultimate step for any separation. However, when the adsorptive species are very similar in size, thermodynamic equilibrium separation could be advantageous since it benefits from the precise positioning of the guest molecules on the binding sites for selective uptake and the demand for the pore size control is less stringent.

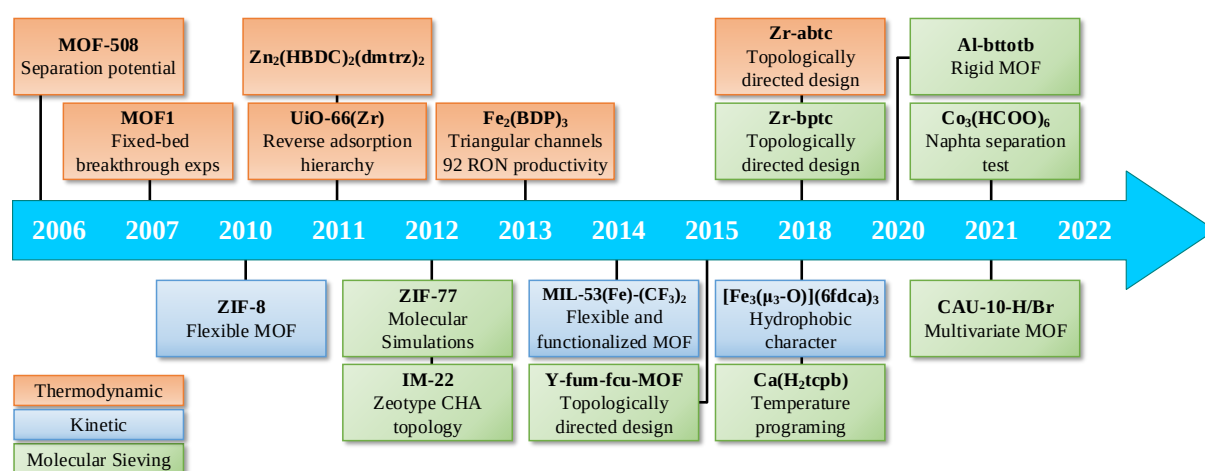


Figure 2.1 | Timeline of significant breakthroughs for MOFs in the field of pentane and hexane isomer separation.

2.2.1 Thermodynamic Separation

2.2.1.1 Normal Adsorption Hierarchy

The first experimental work using a MOF material to separate alkane isomers was reported by Chen et al.⁴⁸ in 2006. A microporous zinc-based, $\text{Zn}(\text{BDC})(4,4'\text{Bipy})_{0.5}$ (MOF-508; BDC = 1,4-benzenedicarboxylic acid; 4,4'Bipy = 4,4'-bipyridine), has been demonstrated as the stationary phase for the gas-chromatographic (GC) separation of pentane and hexane isomers mixtures. The material exhibits a doubly interpenetrated 3D pillar-layered framework featuring a 1D channel system with a cross-section of 0.40 x 0.40 nm (Figure 2.2a), which could selectively accommodate linear alkanes and discriminate branched alkanes ones. Variable-temperature pulse experiments (393 – 433 K range, Figure 2.2b-e) showed that nC5 could be separated from nC6. Mono-branched iC5 elutes from the column before its linear isomer nC5. Similarly, 2MP runs through the column faster than nC6, while 22DMB, the isomer of hexane with the shortest linear chain, elutes even faster. Thus, mixtures with these five alkanes could also be reasonably separated. The separation was attributed to the different van der Waals interactions arising from the subtle matching of size and shape of the alkanes within the micropores framework. Since the 1D channels are accessible to the linear chains but not to the branched parts of the alkanes, the retention time for an alkane isomer, therefore, mainly depends on the length of the linear part of its carbon chain.

In a followed-up study, Bárcia et al.⁴⁹ achieved the efficient separation of linear nC6 from its branched isomers on a derivative microporous MOF, $\text{Zn}(\text{BDC})(\text{dabco})_{0.5}$ (MOF1; dabco = 1,4-diazabicyclo[2,2,2]octane), which has a 3D pillar-layered framework similar to that of MOF-508, but noninterpenetrated. The structure of this material contains two types of intersecting channels with a cross-section of 0.75 x 0.75 nm along the *a*-axis and 0.38 x 0.47 nm along with the other two directions. The authors speculated that the larger channels would thermodynamically accommodate all molecules, nC6, 3MP, and 22DMB, but the narrow ones would exclusively take up nC6, thus affording its separation. This hypothesis was supported by single and multicomponent fixed bed breakthrough experiments at 313 K. The single component data revealed the sorption hierarchy order $\text{nC6} > 3\text{MP} > 22\text{DMB}$, while nC6 shows stronger van der Waals interactions with the framework due to its long chain, smaller size, and the confinement within the narrow channels. The breakthrough curves with equimolar binary and ternary mixtures further confirmed the capability of MOF1 in well-separating nC6

from its branched isomers 3MP and 22DMB. A year later, Dubbeldam et al.⁵⁰ further examined this material to separate a 13-component mixture of alkane isomers in the pentane/heptane range using configurational-bias Monte Carlo (CBMC) simulations. The multicomponent isotherms predicted at 298 K indicated that, except for 2,3-dimethylpentane (23DMP), alkanes with a lower RON are generally strongly adsorbed over the entire pressure range, while species with a higher RON are only weakly adsorbed. The authors suggested that this resulted because the more flexible linear alkanes can adapt to fill more regions of the MOF, whereas the adsorption of branched alkanes is confined to fewer low-energy sorption sites.

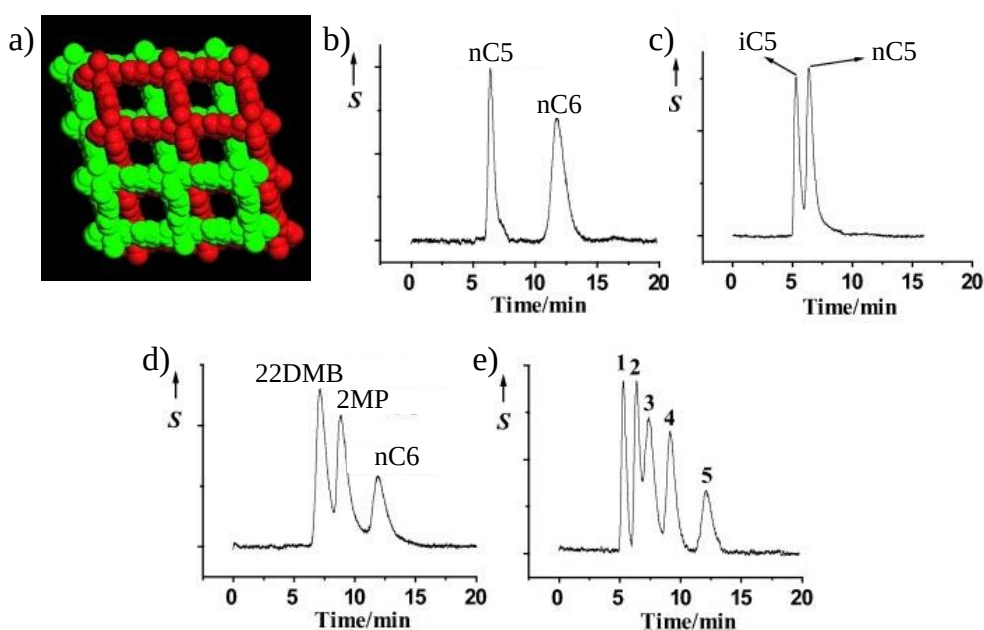


Figure 2.2 | **a)** Space-filling representation of MOF-508 crystal structure. The two interpenetrating frameworks are shown in red and green. **b-e)** Chromatograms for equimolar alkane mixtures in MOF-508 (393 – 433 K range): **b)** nC6/nC5, **c)** nC5/iC5, **d)** nC6/2MP/22DMB and **e)** nC6(5)/2MP(4)/22DMB(3)/nC5(2)/iC5(1). S: thermal conductivity detector response. Adapted from the ref. 48

Based on the works mentioned above, Ling et al.⁵¹ synthesised a new 3D Zn-based pillar-layer structure built on triazole and dicarboxylate linkers for the selective adsorption of linear nC6 and mono-branched 3MP hexanes over their di-branched isomer 22DMB. The microporous MOF, $\text{Zn}_2(\text{HBDC})_2(\text{dmtrz})_2$ (Hdmtrz = 3,5-dimethyl-1H,1,2,4-triazole), exhibit 1D channels with a cross-section of 0.67 x 0.67 nm (Figure 2.3a). Single component adsorption equilibrium isotherms at 298 K revealed that it adsorbs similar amounts for nC6 (13.3 wt.%) and 3MP (12.1 wt.%) but substantially less 22DMB (3.5 wt.%) (Figure 2.3b). To further evaluate the separation capability of the material, a pulse experiment using an equimolar ternary mixture was performed. The results showed that 22DMB was well separated from the other two

isomers, confirming the selective adsorption (Figure 2.3c). Since adsorption kinetics data were not reported, it was not very clear to specify which mechanism governs their adsorption. However, considering the adsorbed amounts from the isotherms, it is reasonable to speculate that: 1) the separation was achieved via a thermodynamically controlled mechanism through different van der Waals interactions, or 2) the separation resulted from both thermodynamic and kinetic effects in which the bulkier 22DMB may encounter some diffusional restrictions under these experimental conditions.

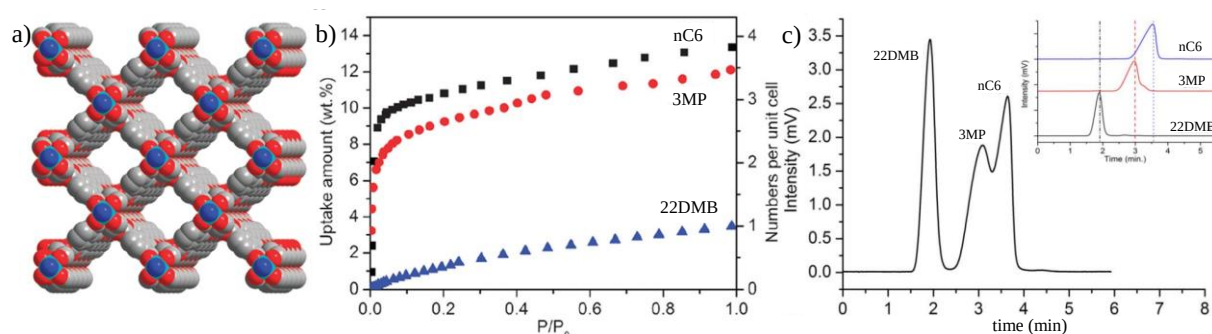


Figure 2.3 | **a)** Space-filling representation of $\text{Zn}_2(\text{HBDC})_2(\text{dmtrz})_2$ crystal structure. **b)** Single component adsorption equilibrium isotherms of hexane isomers in $\text{Zn}_2(\text{HBDC})_2(\text{dmtrz})_2$ at 298 K. **c)** Chromatogram for an equimolar ternary mixture of hexane isomers in $\text{Zn}_2(\text{HBDC})_2(\text{dmtrz})_2$ at 323 K. Adapted from the ref. 51

Herm et al.⁵² reported a microporous MOF $\text{Fe}_2(\text{BDP})_3$ ($\text{BDP}^{2-} = 1,4\text{-benzenedipyrazole}$) that could efficiently separate all the five hexane isomers into practically valuable fractions according to the degree of branching. The material is built on octahedral iron(III) centres linked via pyrazolate units to form a 3D framework comprising 1D triangular channels with suitable dimensions, 1.32 nm edge length and 0.49 nm pore size (Figure 2.4a), which could accommodate all molecules. The experimental single component adsorption equilibrium isotherms measured at high temperatures (403 – 473 K range) showed that $\text{Fe}_2(\text{BDP})_3$ adsorbed similar uptakes for all the isomers but with different adsorption strength, with the calculated isosteric heats following the order of $\text{nC6} > 2\text{MP} > 3\text{MP} > 23\text{DMB} \approx 22\text{DMB}$. In addition, a fixed bed breakthrough experiment with an equimolar quinary mixture at 433 K demonstrated the ability of $\text{Fe}_2(\text{BDP})_3$ to discriminate them into three fractions. The di-branched isomers 22DMB/23DMB eluted first, followed by the mono-branched ones 3MP/2MP, and finally, the linear nC6, leading to a 92 RON ideal productivity of $0.54 \text{ mol} \cdot \text{dm}^{-3}$ (Figure 2.4b). Further CBMC simulations revealed that the molecular separation arises from the varying abilities of the hexane isomers to wedge along the triangular corners of the structure. The 1D channels

provide greater contacts for nC6 to afford strong van der Waals interactions, while the contacts are not maximised for the more compact 23DMB and 22DMB. Through a comparison with published data and additional CBMC simulations, the authors highlighted the superior performance of the $\text{Fe}_2(\text{BDP})_3$, where its 92 RON ideal productivity calculated on a volume basis of the material (framework density) is higher than the values obtained for the other adsorbents (Figure 2.4c). However, despite the potential for separating hexane isomers, $\text{Fe}_2(\text{BDP})_3$ could not completely discriminate HRON and LRON molecules when subjected to complex feed mixtures of pentane and hexane isomers. Their CBMC data indicated that the HRON mono-branched iC5 (91.5) elutes practically simultaneously with the LRON 2MP (73.5) and 3MP (74.5) mono-branched hexanes (Figure 2.4d). This undesirable near-simultaneous elution will undoubtedly decrease the overall process performance, suggesting that this might not be considered the ideal solution for upgrading the current TIP processes.

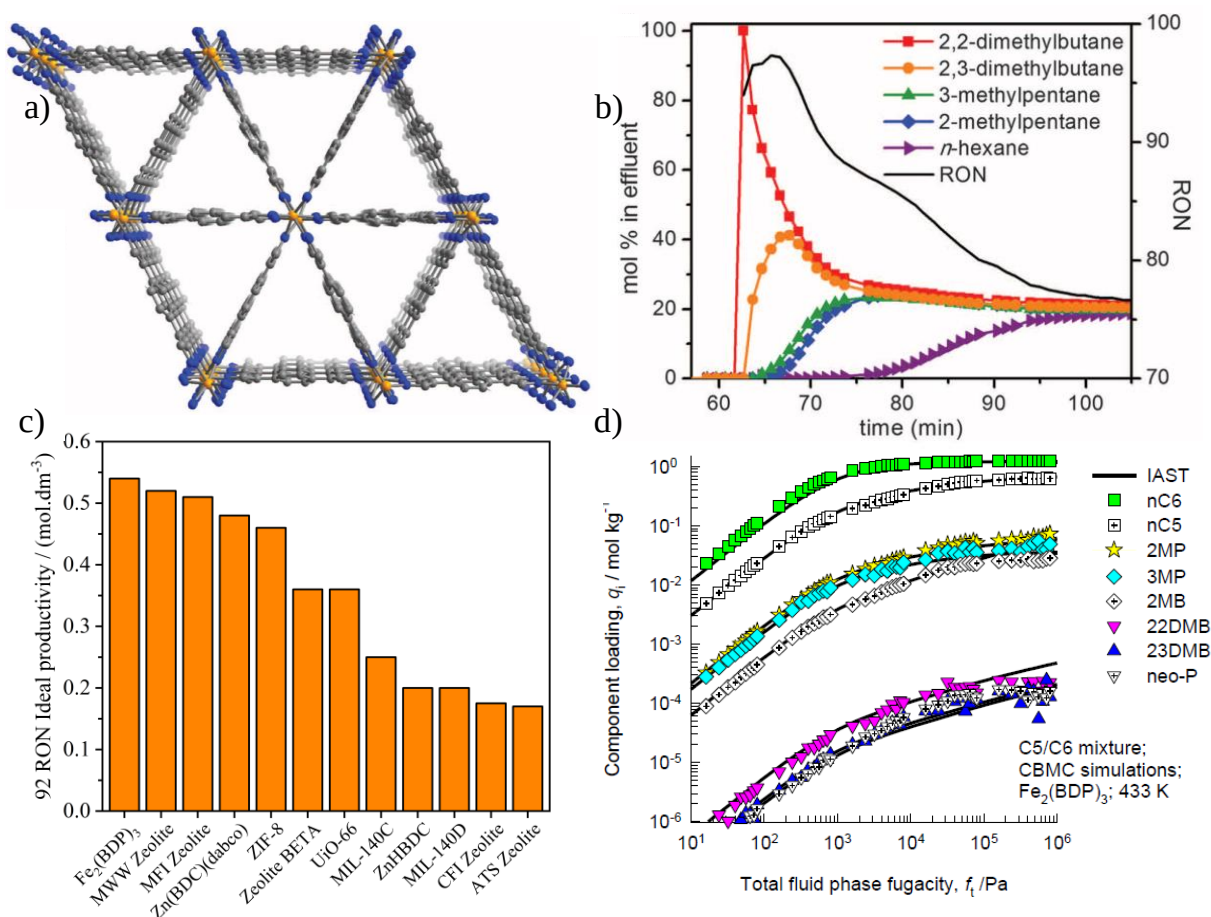


Figure 2.4 | **a)** Crystal structure of $\text{Fe}_2(\text{BDP})_3$. **b)** Breakthrough curves for a quinary equimolar mixture of hexane isomers in $\text{Fe}_2(\text{BDP})_3$ at 433 K. **c)** Simulated 92 RON ideal productivities for the separation of equimolar quinary mixtures of hexane isomers using a variety of materials at 433 K. **d)** Simulated octonary adsorption equilibrium isotherms of pentane and hexane isomers in $\text{Fe}_2(\text{BDP})_3$ at 433 K. Adapted from the ref. 52

Inspired by the separation outcomes from the $\text{Fe}_2(\text{BDP})_3$ material, Wang et al.⁵³ designed and synthesised by reticular chemistry strategy a new Zn-based MOF, $\text{Zn}_9(\text{tba})_9(\text{dabco})_3$ (H_2tba = 4-(1H-tetrazol-5-yl)-benzoic acid), for the separation of hexane isomers. Benefiting from the pre-designed topology and suitable linear linker H_2tba (slightly shorter than BDP^{2-}) and dabco, the material exhibits a 3D framework containing triangular-like and quadrilateral-like channels with an edge length of 1.19 and 0.73 nm, respectively. The fixed bed breakthrough experiments with an equimolar quaternary mixture at 298 K demonstrated an adsorption hierarchy order following the degree of branching, $\text{nC6} > 3\text{MP} > 23\text{DMB} > 22\text{DMB}$, with all isomers being reasonably separated. However, the adsorption behaviour in $\text{Zn}_9(\text{tba})_9(\text{dabco})_3$ is strongly temperature-dependent. At 373 and 423 K, there is a shift in the elution order of hexane isomers, with nC6 eluting first from the column and separated from the branched ones whose elution occurs together. The authors speculated that these outcomes were raised from a synergetic contribution of molecular sieving effect and diffusion rates; however, no sieving effect can be seen from their single component adsorption equilibrium isotherms and even for the multicomponent breakthrough curves. Considering both material properties and experimental data profiles, it seems reasonable to state that the adsorption behaviour in $\text{Zn}_9(\text{tba})_9(\text{dabco})_3$ is controlled by a thermodynamic mechanism based on different host-guest interactions.

Through a high-throughput computational screening over a wide variety of MOF structures contained in the Computational Ready Experimental (CoRE), Chung et al.⁵⁴ indicated that triangular channels with acute corners are not strictly necessary for a high-performing hexane isomers separation material. Moreover, their simulation results demonstrated that linear alkanes do not populate the corners of narrow triangular channels, leading to preferential adsorption, as suggested by Herm et al.⁵² in MOF $\text{Fe}_2(\text{BDP})_3$. Through potential energy surface and three-dimensional siting (density maps) analysis, it was proposed that this separation can also be efficiently achieved in nontriangular pores, such as circular-shaped channels that provide suitable confinement for hexane isomers. The high-throughput computational screening method is a handy tool for simultaneously exploring a large number of MOF structures with topological diversity to draw useful insights to reasonably understand the potential candidate structures. It allows identifying how different performance metrics get affected by the structural properties of the MOFs. Similar investigations were also performed by Peng et al.⁵⁵ and Solanki and Borah.^{56–58}

2.2.1.2 Reverse Adsorption Hierarchy

The examples mentioned above demonstrated the typical sorption hierarchy for alkane isomer separation, which follows the natural order of size and shape selectivity, i.e., the hydrocarbons with linear chains whose kinetic diameter is smaller are preferentially adsorbed over the bulkier ones. Since linear molecules generally pack along with the material's porosity more effectively, their host-guest interactions are maximised. However, this order is not always observed, and an unusual reversed shape selectivity with competitive adsorption in favour of the bulkier species can be obtained. Unlike the adsorption behaviour governed by enthalpy, the reversed sorption hierarchy highlights the contribution of entropy effects, where the guest molecules lose rotational and translational freedom.⁵⁹ For example, straight tubular pore channels might only allow for the translational motion of the molecules, which enables a higher packing efficiency of the shorter molecules (length entropy effect).⁶⁰ In contrast, in systems with cage-like pores, the translational freedom can be severely reduced, and thus, the molecular rotation contribution becomes a determinant factor for the relative adsorption equilibria of molecules with different sizes and shapes (rotational entropy effect).^{59,61}

The first experimental adsorption study of hexane isomers in a microporous MOF, showing a reverse sorption hierarchy, was reported by B rcia et al.⁶² in 2011. The material studied was the UiO-66 (UiO stands for the University of Oslo), a Zr-based MOF built up of $\text{ZrO}_6(\text{OH})_2$ hexanuclear clusters interconnected through bdc linkers to form a cubic rigid 3D pore structure consisting of an array of two types of cages, the octahedral (1.1 nm) and tetrahedral (0.8 nm), accessible via triangular windows with ≈ 0.5 to 0.7 nm (Figure 2.5a). Through fixed bed breakthrough experiments with an equimolar quaternary mixture (343 - 473 K range), the following sorption order was usually obtained $23\text{DMB} > 22\text{DMB} > 3\text{MP} > \text{nC6}$ (Figure 2.5b). Based on the molecular length of the molecules, nC6 (1.06 nm), 3MP (0.93 nm), 23DMB (0.80 nm), and 22DMB (0.80 nm), the authors ascribed that the linear nC6 is too long to be accommodated into the smaller tetrahedral cages. In contrast, the dimensions of bulkier isomers ensure that these molecules are short enough to rotate freely inside the cages, resulting in higher packing efficiency. This experimental reverse selectivity was further corroborated through GC (pulse) experiments,⁶³⁻⁶⁵ immersion calorimetry experiments,⁶⁶ and CBMC simulations.^{52,64,67} Also, decorating the organic linker with different functional groups (-Br, - NH_2 , - NO_2) changes the pore size of the cages and somewhat alters the elution order of the bared UiO-66(Zr).⁶⁸

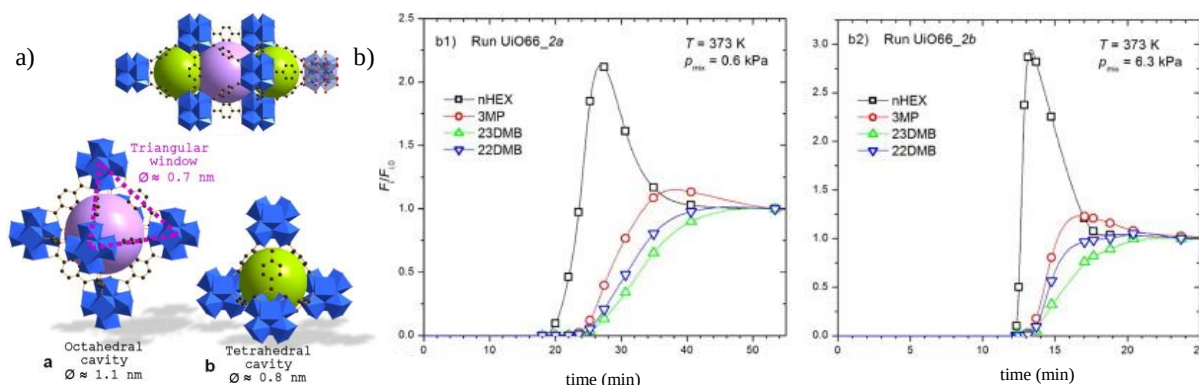


Figure 2.5 | a) View of the octahedral and tetrahedral cages of UiO-66. Zirconium polyhedral and carbon atoms are in blue and black, respectively. **b)** Breakthrough curves for a quaternary equimolar mixture of hexane isomers in UiO-66 at 373 K. Adapted from the ref. 62

The reverse sorption selectivity of hexane isomers, resulting from their differences in rotational freedom, was also observed in the fixed bed breakthrough experiments performed by Peralta et al.⁶⁹ with equimolar binary mixtures at 398 K in the microporous MOF ZIF-76. With the formula $\text{Zn}(\text{Im})_{1.25}(\text{ClbIm})_{0.75}$, the material has the Zn^{2+} cations coordinated to imidazole (Im) and 5-chlorobenzimidazole (HClbIm) linkers. This results in the LTA topology, the same as zeolite 5A, but with larger apertures and cages, which allows the hexane isomers adsorption in the reverse order: $22\text{DMB} > 3\text{MP} > \text{nC6}$. Similar to UiO-66, ZIF-76 is not very selective.

Recently, Bury et al.⁷⁰ reported a rational strategy based on a Cambridge Structural Database search of noncovalent microporous materials (NPM) with a low packing factor to identify a suitable system for the low-energy separation of hexane isomers. This search led to the selection of an oxidotetrazinc cluster based diamondoid NPM network named DiaMM-1, which exhibits two alternating tetrahedral cages, with diameters of 0.75 and 0.91 nm, being accessible through triangular windows of 0.80 nm. Based on that, the fluorinated analogue DiaMM-2 was designed and synthesised, with the size of the cages slightly decreasing to 0.72 and 0.88 nm. The experimental single component adsorption equilibrium isotherms at 293 K revealed that all molecules could access the microporous network. Moreover, at the low-pressure region ($p/p_0 < 0.1$), the more branched molecules were preferentially adsorbed. Variable-temperature pulse experiments (363 – 423 K range), using a senary mixture of pentane and hexane isomers, showed an elution order consistent with the isotherms, it being $22\text{DMB} > 23\text{DMB} > 3\text{MP} > 2\text{MP} > \text{nC6} > \text{nC5}$. According to the authors, this behaviour can be rationalised by preferential loading of the shortest molecules within tetrahedral cages. Comparing both materials, DiaMM-2 gives rise to faster (7 times) and better separation of the alkane mixture.

More recently, Suh and Kim⁷¹ reported through computational simulations that a linker insertion strategy could be used to reconfigure the pore space to introduce a reverse selectivity of the hexane isomers. A size-matching regulated linker (2,4-di(4-pyridinyl)-1,3,5-triazine (dpt)) was inserted into the 1D straight cylindrical channels of Mg-MOF-74 to impose steric effects in the pore structure. The dpt linkers were inserted such that the distance between them is 0.83 nm along with the channel direction, which is lower than the molecular length of linear and mono-branched molecules. Simulated snapshots of the hexane isomers within the channels of dpt-Mg-MOF-74 at 300 K revealed that the reversed selectivity largely comes from nC6 being “stuck” inside the cage created between the two neighbouring dpt linkers. As the branching degree increases, it becomes easier for these branched molecules to rotate vertically and diffuse through the channels. For a linker insertion higher than 40%, the gap in their diffusivities becomes pronounced accordingly $nC6 < 2MP \approx 3MP < 23DMB \approx 22DMB$. The diffusivities of pentane isomers were also computed; however, since they are smaller than the hexane isomers, the linear nC5 was not affected by steric hindrance and the length entropy when passing through the dpt-Mg-MOF-74 channel. Thus, a diffusivity ordering based on their kinetic diameter was obtained, i.e., $iC5 < nC5$.

Although entropy-driven effects can be an alternative way to be explored for separating pentane and hexane isomers, only a very few MOFs experimentally evidenced this reverse sorption behaviour, and they were not very selective. Apparently, better separation performances were found in the high-throughput computational screening literature;^{55–58} however, until now, there is no consistent experimental evidence that can validate the conclusions drawn from these computational simulations.

2.2.2 Kinetic Separation

Flexible MOFs characterise a unique group of materials with “soft” structures that exhibit dynamic structural changes upon external stimuli, such as inclusion and removal of guest molecules, pressure, and temperature. As a result, this structural flexibility can sometimes lead to unexpected adsorption and separation properties. The first experimental evidence for separating pentane and hexane isomers through a kinetic mechanism was observed in the ZIF-8 material, which has a flexible framework exhibiting a zeolitic architecture. Zeolitic imidazolate frameworks are a subfamily of MOFs with extended three-dimensional structures constructed from metal units (e.g., Zn^{2+} , Co^{2+}) bridged together by organic linkers based upon

imidazolate species.⁷² Precisely, the metal units are coordinated by nitrogen atoms at the 1,3-positions of the imidazolate linkers, forming a structure with a metal–imidazole–metal (M–Im–M) angle close to 145° , which is similar to the Si–O–Si angle found in zeolite structures, resulting in frameworks with the same topologies as zeolites. The M–Im–M bond length is longer than that of Si–O–Si, which results in ZIF structures having a larger internal pore diameter. In addition, the bonding between Im and $\text{Zn}^{2+}/\text{Co}^{2+}$ confers exceptional chemical and thermal stability to ZIF structures.⁷³

ZIF-8 has the formula $\text{Zn}(\text{MeIm})_2$, with the Zn^{2+} cations being coordinated to four 2-methylimidazolate linkers (MeIm), resulting in a material featuring a sodalite (SOD)-related zeolite type structure. The sodalite cages (centred at the corners of a cube) possess an internal diameter of 1.14 nm and are accessible through six-membered ring windows with a free aperture equal to 0.34 nm (Figure 2.6a).⁷³ The narrow pore windows were expected to be able to molecular sieve branched alkanes from linear alkanes. In a proof-of-concept study, Chang et al.⁷⁴ applied a ZIF-8 coated capillary as the stationary phase for the GC separation of hexane isomers. A pulse experiment with an equimolar quaternary mixture at 443 K showed a clear separation between nC6 from its branched isomers, 22DMB, 23DMB, and 2MP, though these latter could not be separated from each other (Figure 2.6b). Through various experimentations, the authors concluded that the separation was based on a selective size-exclusion and the negligible retention of branched isomers was believed to be correspondent to the adsorption of the linear part of their hydrocarbon chain. From this work, it is interesting to note the flexible nature of ZIF-8, which did not show a sharp cut-off at 0.34 nm for guest inclusion, allowing the accommodation of larger adsorbate molecules. Nevertheless, more bulky molecules (kinetic diameter > 0.5 nm) could not pass the pore window, leading to a shorter retention time. In a similar study conducted by Luebbers et al.,⁷⁵ the complete separation of pentane isomers was reported following the same mechanism.

After that, Peralta et al.⁶⁹ evaluated the performance of ZIF-8 in separating hexane isomers through fixed bed breakthrough experiments with equimolar binary mixtures at 398 K. Results demonstrated that ZIF-8 could effectively separate linear from branched isomers (nC6/3MP or nC6/22DMB) and also partially discriminate the branched molecules (3MP/22DMB, Figure 2.6c), with 3MP being adsorbed. Based on the working conditions applied (temperature: 398 K, total alkane pressure: 13.3 kPa, contact time: 20 s) and guided by breakthrough simulations, the authors concluded that, contrary to bulkier 22DMB, which is sterically excluded from the pores of ZIF-8, 3MP is just at the edge of the cut-off; i.e., its

adsorption could be possible but subject to strong diffusional limitations. According to its adsorbed amounts (0.41 mol.kg^{-1} and 0.84 mol.kg^{-1} for the systems nC6/3MP and 3MP/22DMB, respectively), they believed that the 3MP adsorption was not only at the pore mouth, but instead, it genuinely entered into the sodalite cages. In addition to diffusional limitations, 3MP was also thermodynamically less-favoured than nC6. This work demonstrated that the flexibility of the ZIF-8 windows is much higher than anticipated by Chang et al.⁷⁴ and is comparable to the kinetic diameter of mono-branched alkanes (0.50 nm). Moreover, ZIF-8 showed significantly higher adsorption capacity and faster mass transfer than zeolite 5A. These breakthrough experiments were reproduced nearly quantitatively by CBMC molecular simulations.^{52,67}

Mendes et al.⁷⁶ also evaluated the performance of ZIF-8 through fixed bed breakthrough experiments (313 - 423 K range). However, in contrast to Peralta et al.,⁶⁹ the breakthrough measurements with equimolar binary (3MP/22DMB) and ternary (nC6/3MP/22DMB, Figure 2.6d) mixtures showed no separation of branched isomers, with both components eluting from the column practically at the same time as that of the blank run experiments. Only the efficient isolation of nC6 was observed, achieving a high working capacity of up to 25 wt.%. The authors stated that this divergence arose from the shorter contact time between the gas mixture and the adsorbent inside the column in their experiments, ranging from 1 to 4 s. Since 3MP is a slow diffusing species, its time constant of diffusion is higher than the provided gas residence time. A similar picture was reported by Zhang et al.,⁷⁷ whose fixed bed breakthrough experiments with equimolar binary mixtures showed a complete separation of pentane isomers, where the branched iC5 practically come out of the bed at the very beginning of the experiments, while the linear nC5 was retained for a substantially longer time.

Differently, Ferreira et al.⁷⁸ investigated the adsorption of hexane isomers on ZIF-8 under static conditions. The single component adsorption equilibrium isotherms at 373 K, measured using a manometric system coupled with a micro-calorimeter, revealed the adsorption of nC6, 2MP, and 23DMB, while 22DMB was practically excluded (Figure 2.6e). The effective trapping of the 23DMB molecule demonstrated that the pore size of ZIF-8 reaches 0.56 nm, which again is higher than the anticipated values. Further computational analysis indicated that the well-established cage-blocking strategy was required to accurately reproduce the experimental observations on the molecular simulations. Zhang et al.⁷⁹ also evaluated the adsorption of hexane isomers under static conditions (uptake system), and a different picture was obtained. The single component adsorption equilibrium isotherms at 323 K showed a

reverse hierarchy order $23\text{DMB} > 2\text{MP} > \text{nC6}$, with the branched alkanes being slightly preferentially adsorbed (Figure 2.6f). Interestingly, this trend is consistent with the molecular simulations performed by Ferreira et al.⁷⁸ in the scenario in which no cage-blocking strategy was applied. It was speculated that entropic effects might favoured the packing of branched molecules. However, the estimated diffusional parameters from the adsorption uptakes revealed diffusion selectivities for $\text{nC6}/3\text{MP}$, $\text{nC6}/23\text{DMB}$, and $3\text{MP}/23\text{DMB}$ of 20, 54, and 3, respectively. This led the authors to conclude that ZIF-8 is capable of kinetically separating not only branched alkanes from nC6 but also di-branched from mono-branched isomers.

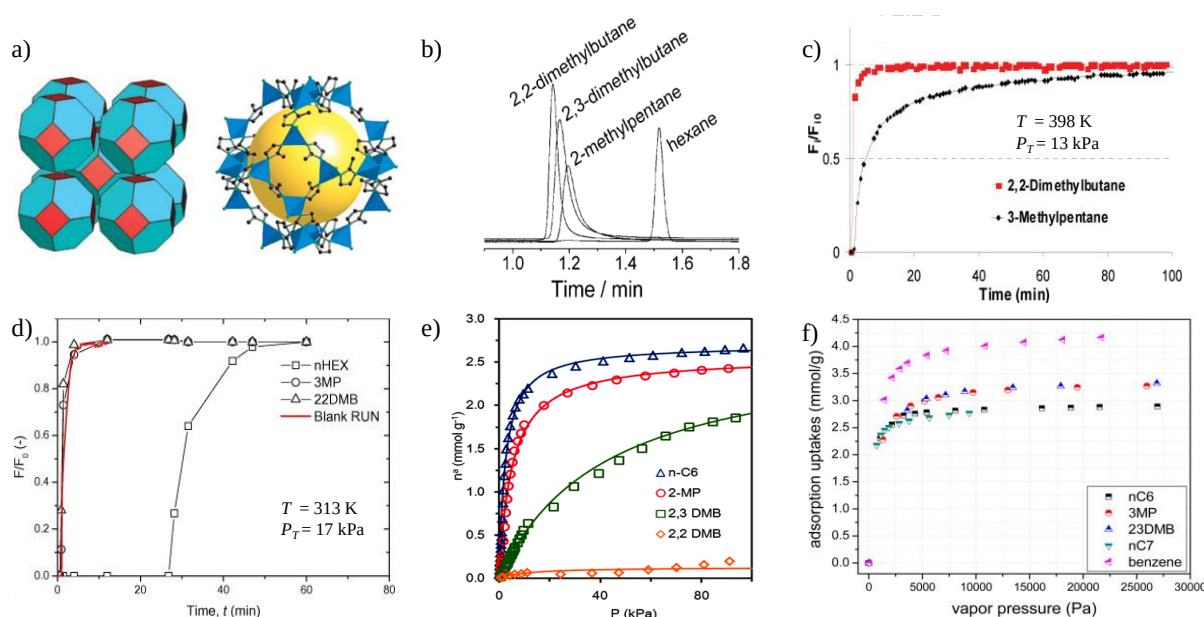


Figure 2.6 | **a)** Left: crystal structure of ZIF-8 as a tiling diagram. Right: ZIF-8 cage with ZnN₄ tetrahedra in blue. **b)** Chromatogram for an equimolar quaternary mixture of hexane isomers in ZIF-8 at 443 K. **c-d)** Breakthrough curves for equimolar mixtures of hexane isomers in ZIF-8: **c)** 3MP/22DMB at 398 K and **d)** nC6/3MP/22DMB at 313 K. **e-f)** Single-component adsorption equilibrium isotherms of hexane isomers in ZIF-8 at: **e)** 373 K and **f)** 323 K. Adapted from the refs. 73, 74, 69, 76, 78, 79, respectively.

The studies mentioned above demonstrated that experimental results of alkane isomers adsorption in ZIF-8 measured under dynamic (continuous flow) or static (batch equilibrium) conditions can be completely different. Indeed, it is noteworthy that it is possible to completely separate linear from its branched alkanes isomers, while equilibrium isotherms show similar uptakes for most of them. These differences may relate to kinetic considerations proper of transient fixed bed adsorbers where the contact time between the gas and the adsorbent is considerably lower, not favouring the adsorption of branched isomers. However, the data from these works suggests that, if the experimental conditions are carefully set up, it might be

possible to split a considerable portion of di-branched from mono-branched hexanes under dynamic conditions by taking into account the differences in their diffusion rates. Therefore, to better understand the influence of these parameters on the adsorption behaviour of alkane isomers and give insights into their adsorption mechanisms, we decided to systematically evaluate this material, being this study presented in *Chapter 4*.

Mendes et al.⁸⁰ reported a kinetically controlled molecular sieve separation of the di-branched 22DMB from its isomers 3MP and nC6 on the flexible and functionalised microporous iron(III) dicarboxylate MIL-53(Fe)-(CF₃)₂. The pristine iron terephthalate MIL-53(Fe) has a 3D framework comprising 1D lozenge channels, whose flexibility involves a reversible shift between the narrow (0.42 nm) or large pores (0.76 nm) forms. The linker functionalisation with bulky perfluoro -CF₃ groups narrowed down the pore aperture of the large pores form of MIL-53(Fe)-(CF₃)₂ to 0.56 nm (Figure 2.7a). These pore sizes were accurately tuned to range below the kinetic diameter of the 22DMB (0.62 nm) and remain close to the dimensions of both nC6 (0.43 nm) and 3MP (0.50 nm) molecules. While it could adsorb similar amounts of pure nC6, 3MP, and 22DMB under equilibrium conditions, due to the flexibility of the framework, remarkable separation under multicomponent conditions was obtained (Figure 2.7b-c). Through a fixed bed breakthrough experiments using an equimolar ternary mixture at 313 K, a complete separation of the 22DMB from the isomeric mixture was achieved, with an elution practically similar to the one obtained during the blank experiments. This observation demonstrated that the 22DMB was not adsorbed within the material's porosity. Further experimental and computational analysis evidenced that the separation was kinetically controlled, as 22DMB showed slower adsorption rates under such conditions. Unfortunately, the adsorption behaviour of hexane isomers in MIL-53(Fe)-(CF₃)₂ is strongly temperature and pressure-dependent, and the separation performance becomes less effective by raising these parameters. Nevertheless, MIL-53(Fe)-(CF₃)₂ represents the first material to exhibit such separation behaviour through a kinetic molecular sieving effect, which provided some clues on making use of flexible MOFs to achieve challenging industrial separations, thus opening a new route in this field of “soft” materials.

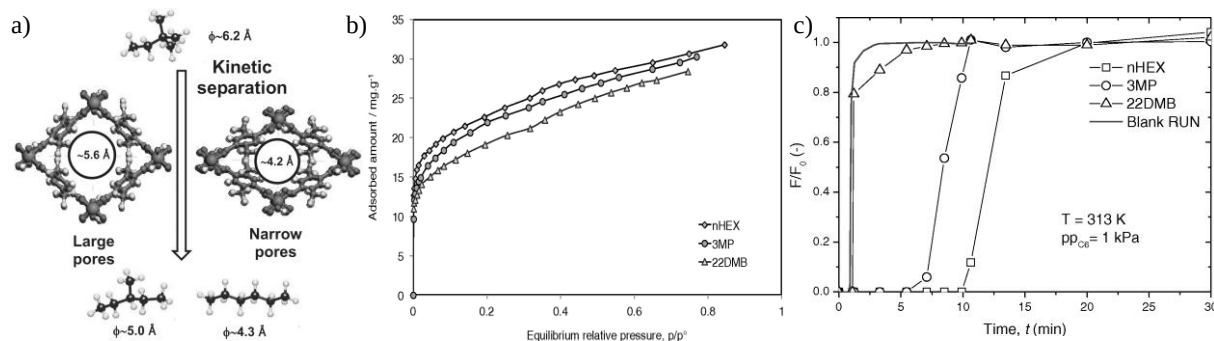


Figure 2.7 | **a)** Illustration of the three hexane isomers with their kinetic diameters and the 1D pore channel of MIL-53(Fe)(CF₃)₂ and their corresponding pore sizes. **b)** Single component adsorption equilibrium isotherms of hexane isomers in MIL-53(Fe)(CF₃)₂ at 313 K. **c)** Breakthrough curves for a ternary equimolar mixture of hexane isomers in MIL-53(Fe)(CF₃)₂ at 313 K. Adapted from the ref. 80

Similar to the introduction of active -CF₃ groups into the pore channels, Lv et al.⁸¹ synthesised the iron-based material, [Fe₃(μ₃-O)](6FDCA)₃, by making the use of preformed building blocks [Fe₃(μ₃-O)(CH₃COO)₆] and organic linker 6FDCA (2,2-bis(4-carboxyphenyl)-hexafluoropropane). The coordination between each trinuclear iron cluster and 6fdca defines a 3D framework with quadrilateral channels of 0.8 x 1.29 nm in size. The high density of fluorine atoms in the channels renders to material excellent chemical stability in aqueous solutions and hydrophobic nature. The single component adsorption equilibrium isotherms at 298 K indicated that the material could accommodate all three studied hexane isomers, nC₆, 2MP, and 22DMB. However, their kinetic adsorption curves revealed an adsorption rate much slower for 22DMB than for the others. To further evaluate this difference in adsorption rates under dynamic conditions, a series of fixed bed breakthrough experiments with equimolar binary mixtures were performed, from where it was highlighted the material's ability in separating linear from branched isomers. This work indicated a possible way to improve the hydrophobicity character and water stability in MOF materials.

2.2.3 Molecular Sieving Separation

Molecular sieving separation is often deemed as the ideal option over thermodynamically or kinetically controlled separation since it offers the highest selectivity. This is the reason why zeolite 5A has been used as a benchmark material for the industrial separation of alkane isomers in the TIP processes. However, separating mixtures through this mechanism has a stringent requirement for subtle matching of the pore structure of the adsorbent with the size (kinetic diameter) or shape (3D dimension) of the adsorptive species.

In this line of thinking, some unique strategies belonging to the MOFs family have been deeply explored to design a suitable material for separating pentane and hexane isomers. These include: i) the judicious selection of appropriate inorganic clusters and organic linkers to obtain rigid framework structures with optimal pore characteristics; ii) designing MOFs with structural flexibility to external stimuli; and iii) fine-tuning the pore size through topologically directed material design rationale or via mixed-linker strategy, etc. Based on these powerful strategies, a number of MOFs with particular molecular sieving properties toward alkane isomers have been obtained.

In 2012, computer simulation techniques were employed by Dubbeldam and co-workers⁶⁷ to screen more than 100 nano-porous structures (zeolites and MOFs) regarding their ability to separate alkane isomers mixtures (pentane - heptane range) at 433 K. Among all the examined structures, the authors highlighted the superior separation performance of ZIF-77, which could fractionate the hexane isomers individually based on the degree of branching, following the order: nC6 > 2MP > 3MP > 23DMB > 22DMB (Figure 2.8a). ZIF-77 has the formula $\text{Zn}(\text{nIm})$, with the Zn^{2+} cations being coordinated to two 2-nitroimidazole linkers (nIm). The material exhibits a highly non-cylindrical structure containing a 2D square channel system (0.45 nm in size) with larger main channels and smaller side channels, from where the separation arises. The larger main channels size-exclude the di-branched molecules, and the smaller channels size-exclude the mono- and di-branched. The 22DMB is too bulky to enter the pore system. Therefore, the material acts as a molecular sieve. Despite showing great potential in separating hexane isomers mixtures, ZIF-77 is a rarely discussed MOF, and to date, there is no experimental data on isotherms or fixed bed breakthroughs measurements that can validate the outcomes from the CBMC simulations. Furthermore, the material apparently suffers from the same drawback seen in the $\text{Fe}_2(\text{BDP})_3$,⁵² which is the simultaneous presence of HRON iC5 with the LRON fraction of mono-branched hexanes. The simulated pulse-style breakthrough curves for a 13-component mixture of all the pentane/hexane/heptane isomers shows that iC5 and 3MP peaks overlap (Figure 2.8b).

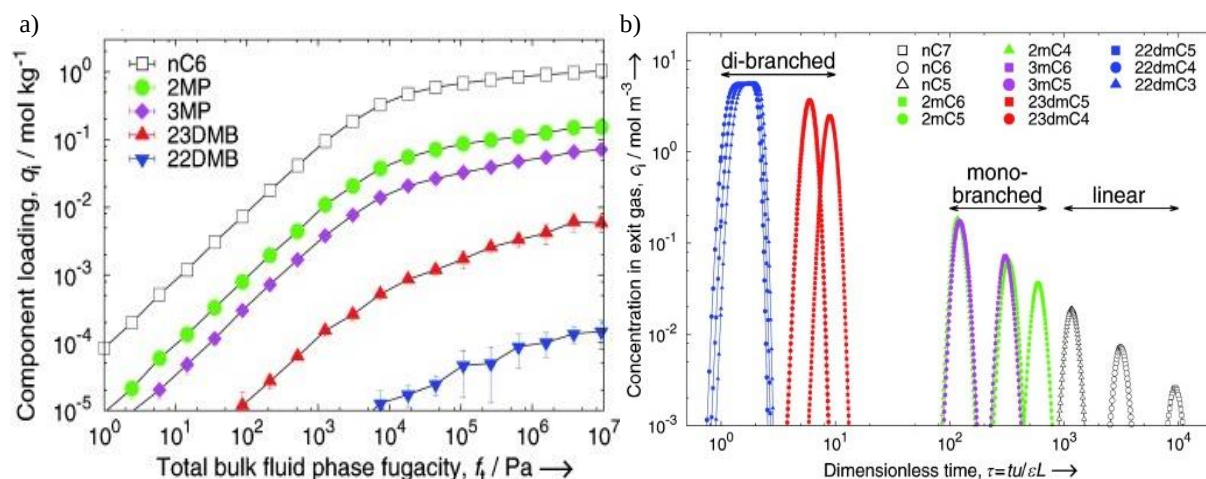


Figure 2.8 | **a)** Simulated adsorption equilibrium isotherms for a quinary equimolar mixture of hexane isomers in ZIF-77 at 433 K. **b)** Simulated pulse-style breakthrough curves for a 13-component equimolar mixture of pentane/hexane/heptane isomers in ZIF-77 at 433 K. Adapted from the ref. 67

Meanwhile, Peralta et al.⁶⁹ reported the synthesis of a new ZIF material called IM-22, a solid containing an inorganic network of metal centres based on Zn^{2+} cations connected together by two organic imidazolate linkers, MeIm and HClbIm. IM-22 represents the first solid among the ZIF series displaying the zeotype CHA topology, a cage-based system accessible through six-membered rings windows. Fixed bed breakthrough experiments with equimolar binary mixtures at 398 K showed that the linear nC6 and mono-branched 3MP could diffuse quite freely into the material porosity. At the same time, the di-branched 22DMB was excluded, breaking practically immediately. The material revealed a slightly slower adsorption capacity than zeolite 5A but displayed fast mass transport, which might still lead to better productivity.

In another early report, Mendes et al.⁸² conducted an experimental screening in a series of rigid porous metal (III/IV) carboxylate-based MOFs with different compositions and topologies for hexane isomers separation. Specifically, MIL-100(Cr), MIL-127(Fe), and MIL125(Ti)- NH_2 were evaluated, from where it was found that MIL-127(Fe) could separate the linear nC6 from its branched isomers through a molecular sieving mechanism. The material exhibits a 3D framework comprising two types of pores, namely an accessible 1D channel system with ≈ 0.6 nm and cages (≈ 1.0 nm) accessible through very narrow windows of ≈ 0.3 nm. The fixed bed breakthrough experiments with an equimolar quaternary mixture (343 - 423 K range) revealed that only nC6 could access the 1D channels, while 3MP, 23DMB, and 22DMB spontaneously eluted from the column at the beginning of the experiments. Furthermore, the nC6 breakthrough profiles show a simple approach to equilibrium, meaning that for this alkane, the adsorption is mainly controlled by a strong resistance to mass transfer. The authors

suggested that the Cl^- counter anions within the channels significantly reduced the hexane accessibility, allowing only the slow diffusion of nC6 with adsorbed amounts reaching a maximum of 7 wt.%.

Eddaoudi et al.⁸³ have successfully applied the isorecticular chemistry approach to ultra-tune the aperture size of a series of rare earth metal-based MOFs with fcu topology (RE-fcu-MOFs) to obtain a microporous material for steric separating linear from branched isomers. The fcu-MOFs possess two types of cages, one with an octahedral shape and the other with a tetrahedral shape whose faces comprise triangular windows (delimited by the organic linkers) constituting the sole access for guest molecules. To fine-tune the aperture size of these windows while keeping the underlying topology of the material intact, the authors systematically choose different organic linkers with similar functionality but decreasing molecular length. More specifically, 2-fluoro-4-(1H-tetrazol-5-yl)benzoate (H_2FTZB), 1,4-naphthalenedicarboxylate (1,4-NDC), and fumarate (fum), with the sizes of 0.84, 0.69, and 0.50 nm respectively. As a result, targeted RE-fcu-MOFs revealed windows with an accessible pore aperture of 0.60, 0.50, and 0.47 nm, respectively, which are closely related to the length of the organic linkers (Figure 2.9a). The judicious choice of the shortest linker fumarate allowed to isolate the new MOF (Y-fum-fcu-MOF) with a contracted pore size that falls right between the kinetic diameters of alkane isomers, being slightly larger than linear paraffins (0.43 nm) and shorter than most branched paraffins (0.50 nm). The single component adsorption equilibrium isotherms at 293 K demonstrated that this MOF could adsorb linear alkanes but fully excluded their branched isomers, resulting in separation through selective molecular exclusion (Figure 2.9b-c). Moreover, a fixed bed breakthrough experiment with an equimolar binary mixture of butane isomers confirmed this full sieving. The iso-butane (iC4) eluted from the column immediately while the linear butane (nC4) was retained for a substantially longer time (Figure 2.9d). Experiments on Y-1,4-NDC-fcu-MOF showed identical adsorption equilibrium amounts of the pentane isomers for the entire pressure range but with faster adsorption kinetics for nC5, indicating a kinetically controlled mechanism. For the longest linker, H_2FTZB , it is expected that all molecules can be adsorbed without noticeable diffusional limitations.

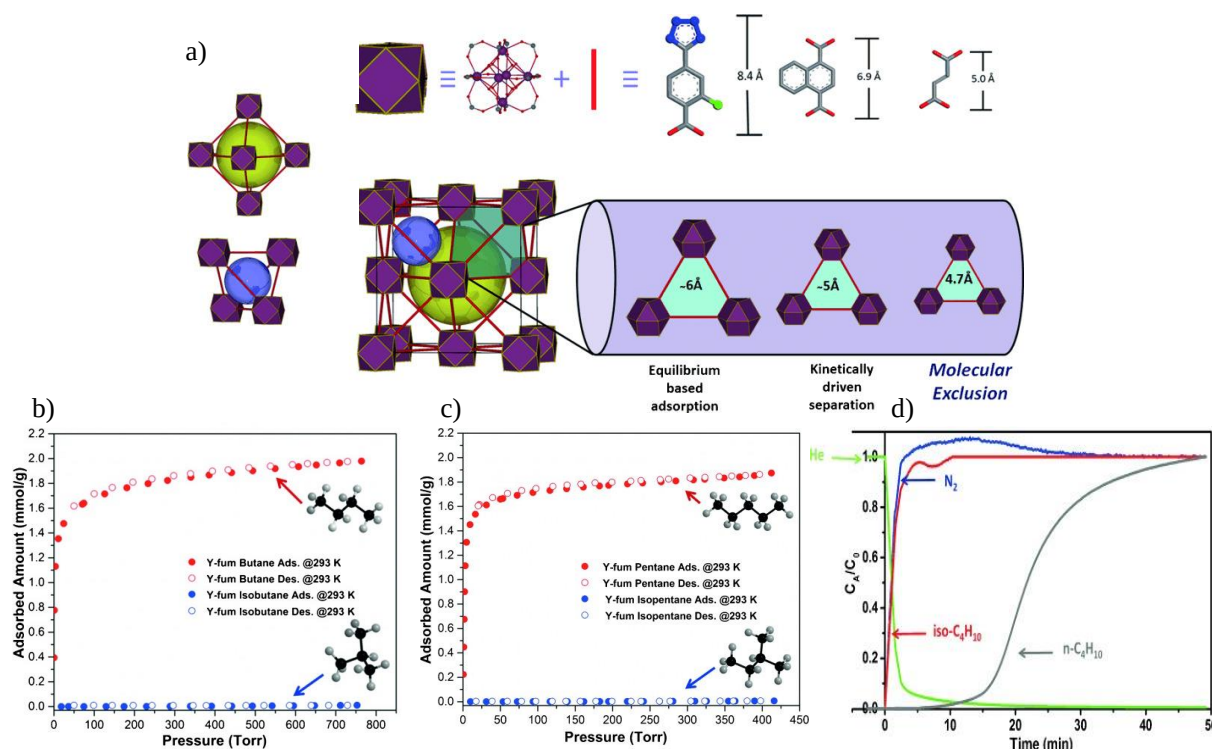
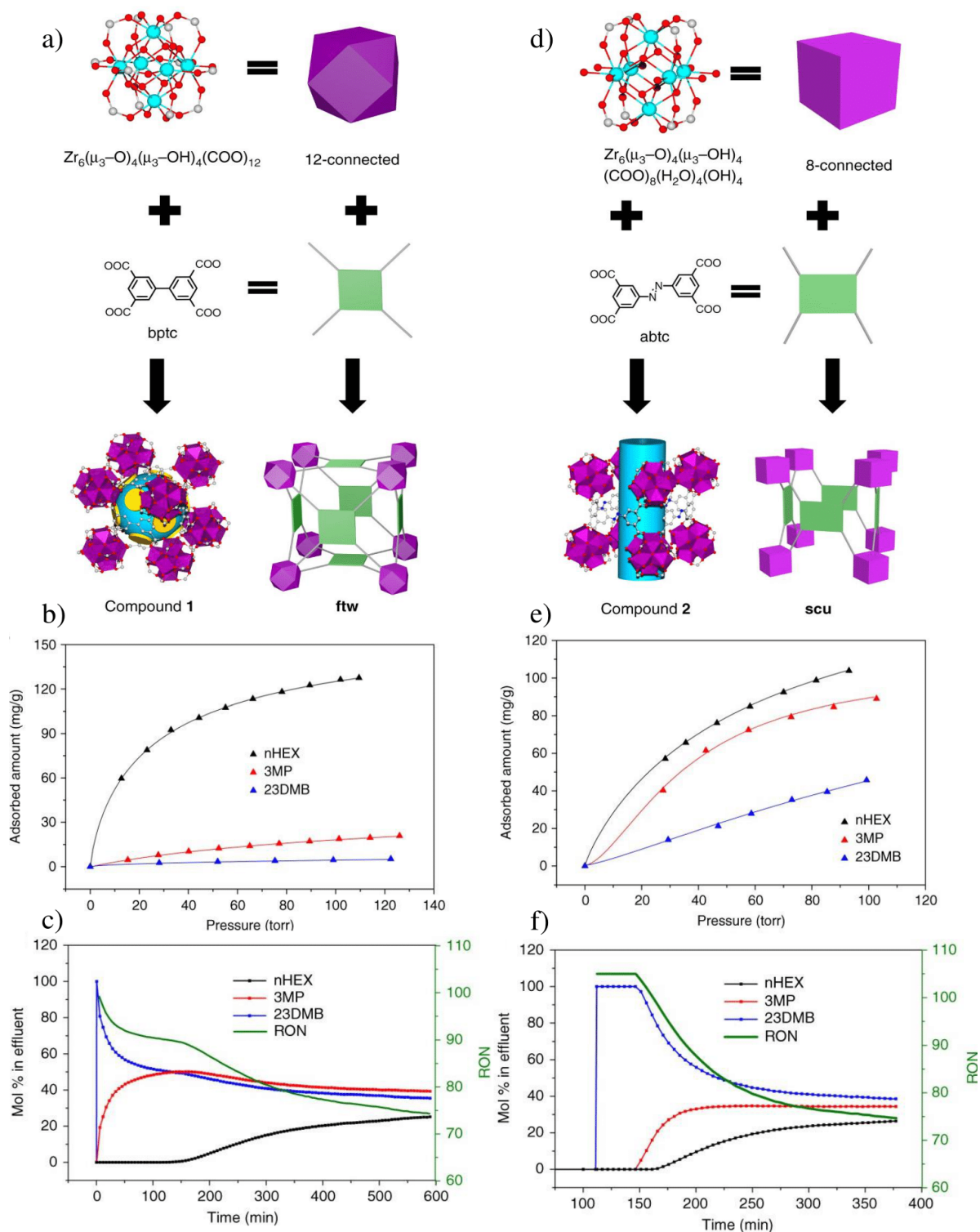


Figure 2.9 | **a)** Structure analysis of RE-fcu-MOFs platform. **b-c)** Single component adsorption equilibrium isotherms in Y-fum-fcu-MOF at 293 K: **b)** butane isomers and **c)** pentane isomers. **d)** Breakthrough curves for a binary equimolar mixture of butane isomers in Y-fum-fcu-MOF at 293 K. Adapted from the ref. 83

Apart from the above-mentioned fcu-type structures, MOFs with ftw topology represent another group of materials for which the reticular chemistry approach has been well implemented.⁸⁴ MOFs with ftw topology are typically built on 12-connected hexanuclear SBUs (Zr₆, Hf₆, Y₆, Ni₆) and 4-connected square-shaped (or rectangular) tetra-functional (usually tetracarboxylates) linkers to form a 3D porous framework with large cubic cages-like pores connected through small windows. The large cages ensure high adsorption capacity, while the small windows can act as “gates” to split or discriminate different adsorbates based on their molecular sizes/shape. Additionally, the window’s size is essentially dominated by the distance between adjacent carboxylates of the organic linkers.⁸⁴ Therefore, concerning sieving property control, it is possible to fine-tune the pore size in an ftw-type MOF by carefully adjusting the organic linker’s dimension that fits into the topology.

Keeping this in mind, Wang et al.⁸⁵ reported a topologically-directed design and synthesis of a series of Zr-based MOFs through a deliberate selection of iso-phthalate-based tetratopic linkers with appropriate molecular dimensions to afford optimised pore structures for the efficient separation of hexane isomers. With the smallest linker, 3,3',5,5'-biphenyltetracarboxylate (bptc), the distance of adjacent Zr-SBUs was optimised so that the

pore windows enable the complete separation of linear and branched hexane isomers via selective size sieving. The Zr-bptc features cage-like pores (≈ 1.2 nm) interconnected through smaller tetrahedral cages with a windows size of ≈ 0.45 nm (Figure 2.10a), which are considerably smaller than those of most reported Zr-ftw-MOFs analogues. It is worth mentioning that Zr-bptc possesses exceptionally high thermal and water stability. Experimental single component adsorption equilibrium isotherms at 423 K revealed that Zr-bptc could adsorb nC6 while showing negligible adsorption of 3MP and essentially no uptake of 23DMB (Figure 2.10b). It is worth noting that nC6 achieved an uptake up to 130 mg.g^{-1} , around 70% higher than the benchmark zeolite 5A (77 mg.g^{-1}) under identical working conditions. Such a molecular sieving effect was further confirmed by fixed bed breakthrough experiments with an equimolar ternary mixture, in which branched hexanes spontaneously eluted from the column while the linear nC6 was substantially retained (Figure 2.10c). The authors attempted to tune the pore structure by replacing the bptc with a slightly longer linker, 3,3',5,5'-azobenzene-tetracarboxylate (abtc), with the same geometry and functionality. However, the abtc linker did not give rise to an isorecticular compound due to its larger aspect ratio, making it difficult to fit into the ftw topology. Instead, it featured a scu-type structure with 8-connected SBUs, a derivative net of ftw with organic linkers missing along one direction, which transformed the cage-like pores into 1D channels with ≈ 0.7 nm (Figure 2.10d). Due to its larger aperture, the Zr-abtc material adsorbed all the three isomers following the sorption hierarchy order $\text{nC6} > 3\text{MP} > 23\text{DMB}$ (Figure 2.10e). Besides, it could discriminate them according to the degree of branching via a thermodynamically driven mechanism attributed to their differences in binding affinities with the MOF channels (Figure 2.10f). The 1D channels provide stronger van der Waals interactions for the linear alkane, while for di-branched isomers, these interactions are not maximised as they are not flexible enough for sufficient contact with the channel. Additional computational evidence supported the underlying separation mechanism of both Zr-bptc and Zr-abtc materials.



In the same year, Wang et al.⁸⁶ also demonstrated the complete fractionation of linear nC6, mono-branched 3MP, and di-branched 22DMB isomers into individual components through a temperature programming separation process using a flexible calcium-based microporous $\text{Ca}(\text{H}_2\text{tcpb})$ ($\text{tcpb} = 1,2,4,5\text{-tetrakis(4-carboxyphenyl)-benzene}$). The CaO_6 octahedra are connected through $\text{H}_2\text{tcpb}^{2-}$ linkers to form a 3D framework with 1D channels of ≈ 0.55 nm (Figure 2.11a), which falls between the kinetic diameters of the branched molecules (0.50 – 0.62 nm). The single component equilibrium data for each hexane isomer showed that the adsorption is highly dependent on temperature (relative pressure), and the material exhibits a temperature-dependent size-exclusion separation behaviour (Figure 2.11b-c). At 393 K, it could adsorb only nC6, while at 333 K, it accommodated both nC6 and 3MP but fully excluded 22DMB. However, at the lowest temperature of 303 K, it could adsorb all three hexane isomers. Thus, $\text{Ca}(\text{H}_2\text{tcpb})$ behaves as a molecular sieve for linear and branched hexanes at 393 K, while at 333 K, it sieves 22DMB from the others. These separations were supported by fixed bed breakthrough experiments, where equimolar binary mixtures of nC6/3MP and 3MP/22DMB could be completely separated at 393 and 333 K, respectively (Figure 2.11d-e). Inspired by the temperature-dependent adsorption behaviour of $\text{Ca}(\text{H}_2\text{tcpb})$, the authors designed a temperature-programmed breakthrough system with two columns connected in series, with the first column at 393 K and the other at 333 K. As a result, a clean separation of an equimolar ternary mixture into three chemically pure individual components was obtained (Figure 2.11f). Further structural analysis by x-ray diffraction revealed that the $\text{Ca}(\text{H}_2\text{tcpb})$ framework is flexible, leading to pore size changes at different temperatures and upon guest molecule accommodation. Based on these observations, it was stated that this unique temperature- and adsorbate- dependent adsorption behaviour could be attributed to the combined effect of the alkane's molecular size and the extent of their interaction with the MOF. The authors claimed that $\text{Ca}(\text{H}_2\text{tcpb})$ is the first adsorbent material that shows complete size sieving toward mono- and di-branched alkanes. However, while an ideal selective molecular exclusion separation was achieved, it was limited to a specific range of temperature and pressure, which may not fit the conditions under the current industrial practice.

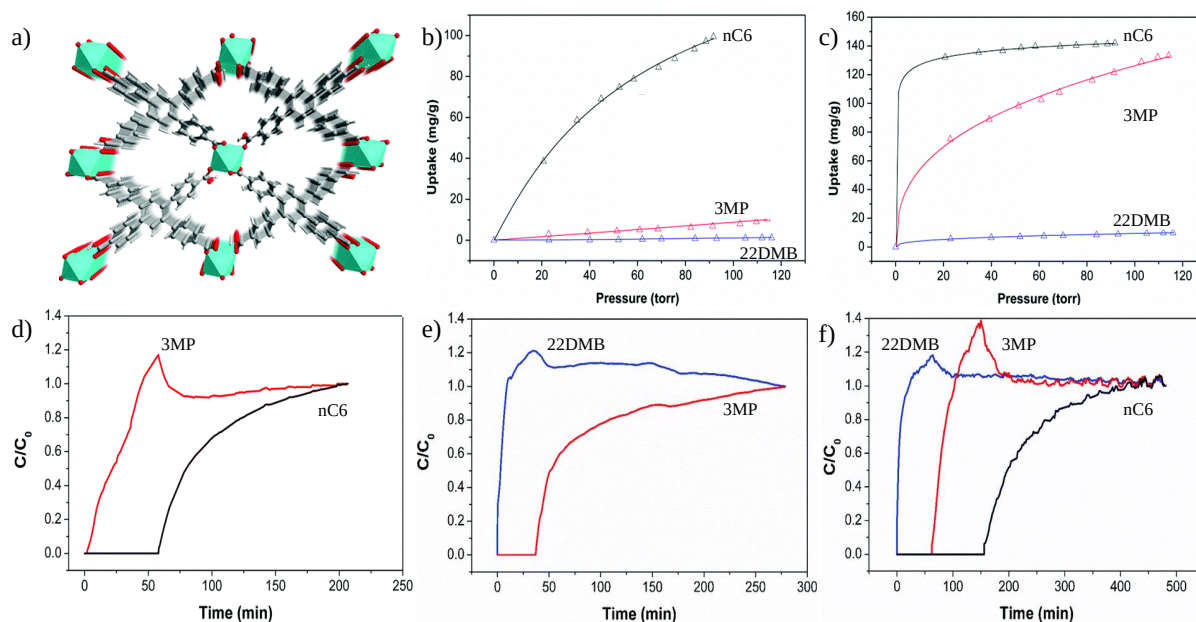


Figure 2.11 | **a)** Crystal structure of $\text{Ca}(\text{H}_2\text{tcpb})$. **b-c)** Single component adsorption equilibrium isotherms of hexane isomers in $\text{Ca}(\text{H}_2\text{tcpb})$ at: **b)** 393 K and **c)** 333 K. **d-f)** Breakthrough curves for equimolar mixtures of hexane isomers in $\text{Ca}(\text{H}_2\text{tcpb})$: **d)** nC6 /3MP at 393 K, **e)** 3MP/22DMB at 333 K, and **f)** nC6 /3MP/22DMB at 393 and 333 K, respectively, in a temperature-programmed two-column system. Adapted from the ref. 86

Recently, Yu et al.⁸⁷ reported the separation of hexane isomers according to the degree of branching at ambient conditions through complete molecular sieving by a robust aluminum-based MOF material, Al-bttotb ($\text{H}_3\text{bttotb} = 4,4',4''\text{-(benzene-1,3,5-triyltris(oxy))tribenzoic acid}$). The AlO_6 polyhedra are connected through bttotb^{3-} linkers to form a 3D framework with two typed of 1D channels with a square-shaped cross-section (Figure 2.12a). Pore size distribution showed that the material has a uniform pore size of 0.56 nm. Single component adsorption equilibrium isotherms at 303 K showed that the material could well accommodate linear nC6 (151 mg.g^{-1}) and mono-branched 3MP/2MP ($94 - 104 \text{ mg.g}^{-1}$) alkanes and showed moderate adsorption for the di-branched 23DMB (42 mg.g^{-1}). However, no adsorption was achieved toward the bulkiest 22DMB (Figure 2.12b). Additionally, their kinetic adsorption curves revealed that 23DMB is adsorbed under certain diffusion restrictions, while 22DMB showed no changes in uptake as equilibrium time increased, suggesting the molecule is fully excluded by the MOF. Fixed bed breakthrough experiments with equimolar mixtures, ternary ($\text{nC6}/3\text{MP}/22\text{DMB}$) and quinary ($\text{nC6}/2\text{MP}/3\text{MP}/23\text{DMB}/22\text{DMB}$, Figure 2.12c), confirmed the Al-bttotb ability in separating hexane isomers into three fractions, linear > mono-branched > di-branched, with 22DMB spontaneously breaking out without any retention. Accordingly, Al-bttotb represents the first MOF material with a rigid framework that shows a clean separation between mono- and di-

branched alkanes through a selective molecular exclusion. Further experimental x-ray diffraction and computational analysis provided information on the underlying separation mechanism at the molecular level, with the selective adsorption behaviour of Al-bttotb toward hexane isomers being attributed to its optimal channel dimensions.

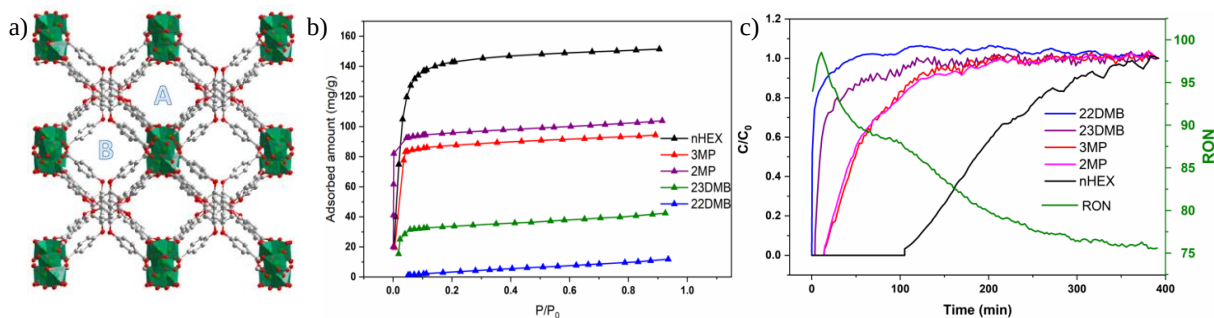


Figure 2.12 | **a)** Crystal structure of Al-bttotb with two types of pore channels (A and B). **b)** Single component adsorption equilibrium isotherms of hexane isomers in Al-bttotb at 303 K. **c)** Breakthrough curves for a quinary equimolar mixture of hexane isomers in Al-bttotb at 303 K. Adapted from the ref. 87

Another robust MOF that demonstrated the ability to separate mono and di-branched hexane isomers at ambient conditions through a molecular sieving mechanism is Co₃(HCOO)₆ (denoted as Co-fa).⁸⁸ The material is built exclusively on Co²⁺ and formate (HCOO⁻), resulting in a 3D framework containing 1D channels with a pore diameter of 0.55 nm (Figure 2.13a). Single component adsorption equilibrium isotherms at 303 K revealed that the compound could adsorb similar amounts of nC₆, 3MP, and 2MP (1.5 – 1.7 mmol.g⁻¹) while showing negligible adsorption for 23DMB and 22DMB (Figure 2.13b). The separation capability of Co-fa was then confirmed by a fixed bed breakthrough experiment with an equimolar ternary mixture. Both nC₆ and 3MP were retained, and 22DMB eluted out from the column at the first minute without any retention (Figure 2.13c). To further give insights into the separation ability of Co-fa, the authors performed a proof-of-concept separation test of naphtha. The refinery naphtha was characterised by a RON value of 69.4 and included C₅-C₁₂ alkanes, cyclo-alkanes, and aromatic hydrocarbons. A column was filled with Co-fa pellets (18.0 g), the naphtha mixture was fed, and the product was subjected to GC analysis. The first drop of the eluted product gave a RON of 85.69, which stayed above 83 until a total amount of 3.26 g was recovered. For comparison, parallel experiments under the same conditions were performed on zeolite ZSM-5 and MOF Al-bttotb, revealing lower RON values for the first drop, 84.2 and 84.1, respectively. Moreover, the product amount collected with RON > 83 also was lower, 0.94 and 2.08 g, respectively. These outcomes indicate that Co-fa has a separation performance that outperforms ZSM-5 and

Al-bttotb materials. To conclude, the authors highlighted that the material could be synthesised at hundred-gram scale in one reaction in lab, which indicates its easy scalability.

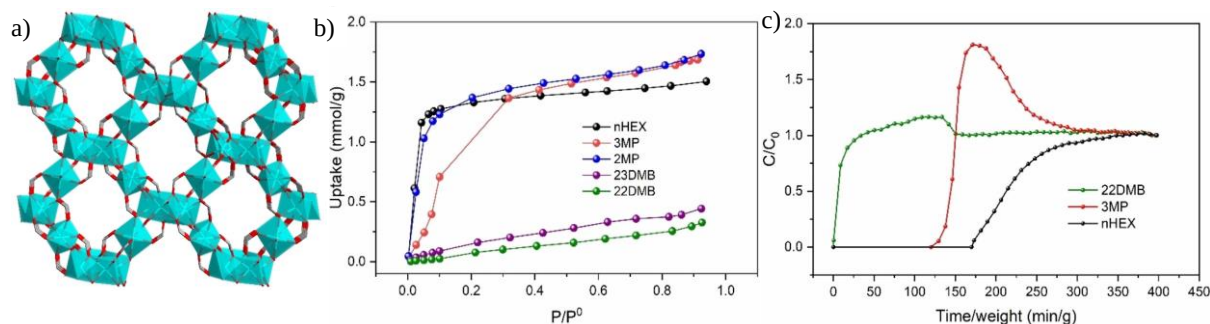


Figure 2.13 | **a)** Crystal structure of Co-fa. **b)** Single component adsorption equilibrium isotherms of hexane isomers in Co-fa at 303 K. **c)** Breakthrough curves for a ternary equimolar mixture of hexane isomers in Co-fa at 303 K. Adapted from the ref. 88

In addition to conventional topologically directed material design based on the organic linkers' length adjustment, the multivariate strategy represents another important approach that allows the precise fine-tuning of the pore environment of a MOF to achieve selective adsorption. Multivariate MOFs (MTV-MOFs) are constructed by mixing organic linkers with the same geometrical parameters and linking groups but featuring different appended substituents precisely positioned.⁸⁹ Therefore, the multivariate strategy can incorporate multiple functional groups into the MOF to optimise its surface properties without changing the underlying framework topology. These heterogeneous materials have been demonstrated to be capable of combining the merits of the pristine MOFs based on their individual organic linkers, leading to synergistic effects between specific combinations of functionalities that result in efficient adsorption separation.⁸⁹

Guided by this strategy, Yu et al.⁹⁰ engineered the pore environment of CAU-10-series MOFs (CAU stands for Christian-Albrechts-Universität) to obtain a mixed-linker MOF that is capable of selective molecular sieving toward alkane isomers. The CAU-10-series is built up from helical chains of *cis* corner-sharing AlO_6 octahedra interconnected by isophthalic acids that bear functional groups in 5-position. This leads to a 3D framework delimiting square-shaped sinusoidal channels with periodic narrow and wide accesses (Figure 2.14a-c). Given the distinct difference in channel size and polarity, the authors selected CAU-10-H and CAU-10-Br as experimental objects. The minimum and maximum channel width of CAU-10-H is around 0.62 and 1.16 nm, respectively, and that of CAU-10-Br is about 0.41 and 1.16 nm, respectively, revealing that the substituents only took up the space of narrow entrances while the maximum

width of channels remained unchanged. According to these dimensions, the authors conjectured that CAU-10-H would be able to accommodate all hexane isomers, in contrast to CAU-10-Br, in which only linear alkanes would get through the narrow channel entrance. Therefore, to only molecular sieve di-branched alkanes, they envisaged that if one of the four isophthalic acids assembling the pore landscape of CAU-10-H was substituted with the 5-bromoisophthalic, the pore size would decrease in a less extent. Along this line of thinking, the mixed-linker MOF denoted as CAU-10-H/Br, was synthesised by a proper ratio of isophthalic acid and 5-bromoisophthalic acid (3:1) featuring narrow channels of 0.54 nm width. The data collected from the single component adsorption equilibrium isotherms at 303 K followed their hypothesis (Figure 2.14d-f). CAU-10-H could accommodate all molecules, CAU-10-Br essentially adsorbed nC6 and yield minimal amounts of 3MP, and as envisaged, CAU-10-H/Br showed adsorption towards nC6 (1.5 mmol.g^{-1}) and 3MP (0.7 mmol.g^{-1}) while practically excluded 22DMB. Additional fixed bed breakthrough experiments with an equimolar ternary mixture at 363 K highlighted the separation performance of the mixed-linker CAU-10-H/Br, which exhibited near exclusion of the di-branched 22DMB while adsorbed the other isomers (Figure 2.14i). Supplementary CBMC simulations and density functional theory calculations revealed the orientations of the hexane molecules in the channels and the adsorption sites for host-guest interaction. The partial appended -Br groups in the channels play a vital role in the steric exclusion of 22DMB and, at the same time, afford strong host-guest interaction for the adsorption of nC6 and 3MP molecules. This work represents the first study in which regulating pore size by MTV-MOFs strategy was successfully applied in hexane isomers separation, providing important clues on using this approach for challenging industrial separations.

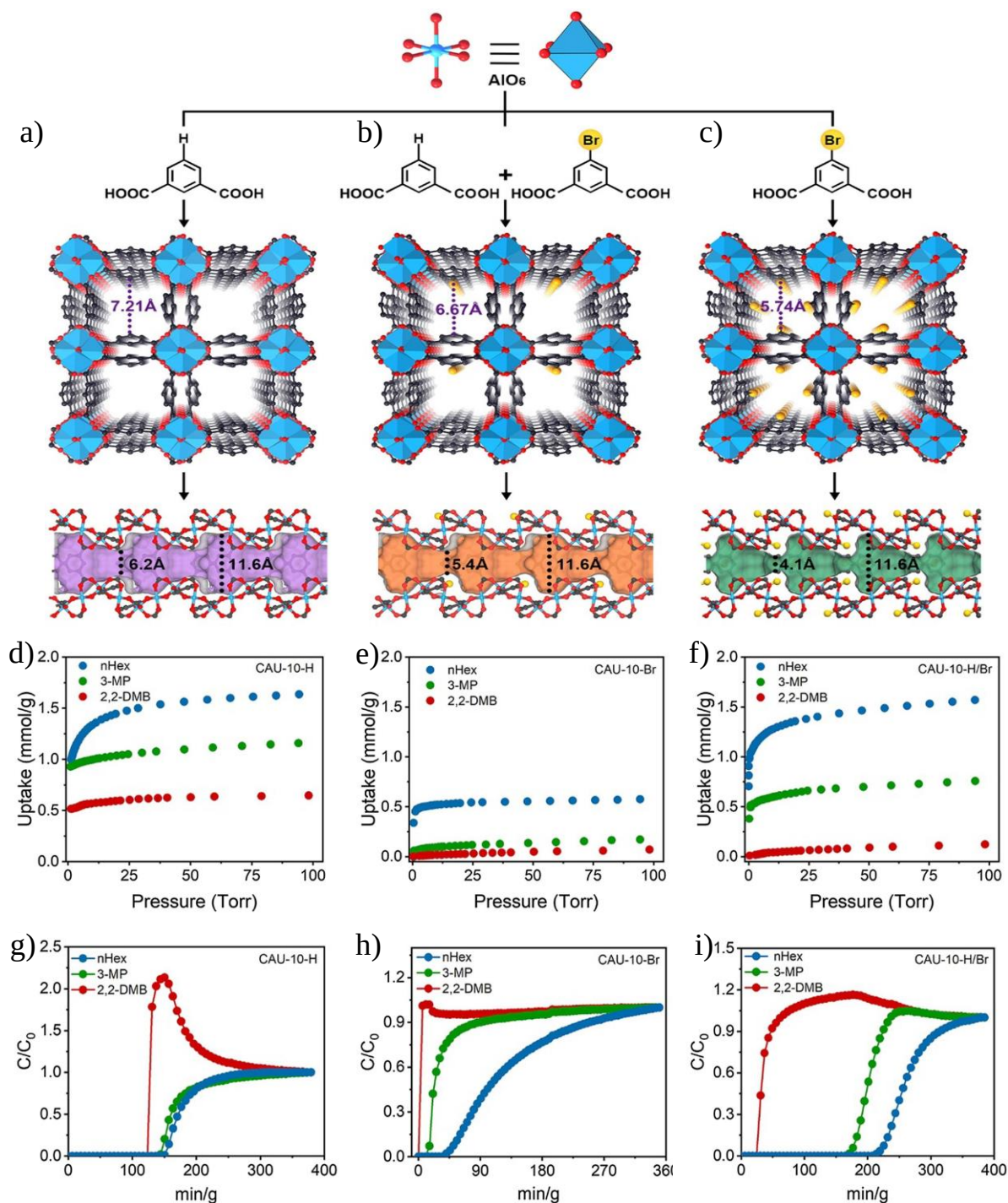


Figure 2.14 | **a-c)** Structure analysis of CAU-10 series materials: **a)** CAU-10-H, **b)** CAU-10-Br, and **c)** CAU-10-H/Br. **d-f)** Single component adsorption equilibrium isotherms of hexane isomers at 303 K in: **d)** CAU-10-H, **e)** CAU-10-Br, and **f)** CAU-10-H/Br. **g-i)** Breakthrough curves for a ternary equimolar mixture of hexane isomers at 363 K in: **g)** CAU-10-H, **h)** CAU-10-Br, and **i)** CAU-10-H/Br. Adapted from the ref. 90

2.3 Conclusions and Outlook

After 15 years since the first experimental report, MOFs have proven to be promising candidates for effectively separating hexane isomers aiming at upgrading gasoline RON. Their modular nature associated with reticular chemistry led to the development of materials whose selectivity performance towards branched alkanes and/or uptake capacity outperformed those from zeolites, including the benchmark zeolite 5A. Although remarkable progress has been made, this research field remains not fully developed, and some specific challenges need to be addressed before a MOF-based alkane adsorptive separation technology can be industrially implemented. Some areas for improvement include:

1) Real system assessment: for real-world applications, significant effort should be made to evaluate the separation performance of MOF materials under working conditions mimicking industrial practice, i.e., with the consideration of the same feed gas of the current process, high temperature, shaped materials, as well as under continuous adsorption/desorption cyclic operation tests. This is essential to assess the materials' capability accurately, as the MOF adsorbents may behave very differently under distinct conditions. Most experimental works highlighted in this chapter (breakthrough measurements) did not use complex pentane and hexane feed mixtures, and only a few even considered all five hexane isomers. A common trend observed in the screening tests reported consists of using one hexane isomer for each degree of branching. However, this might not lead to the true separation performance of the adsorbent material since molecules with the same degree of branching but with different kinetic diameters (di-branched hexanes, 22DMB/23DMB) or carbon number (pentane and hexane mono-branched alkanes, iC5/2MP/3MP) might present very different behaviours. Regarding the temperature, some MOFs ($\text{Zn}_2(\text{HBDC})_2(\text{dmtrz})_2$, MIL-53(Fe)-(CF₃)₂, Al-bttotb, Co-fa, CAU-10-H/Br) either were analysed or showed promising outcomes only at ambient conditions, which does not represent the range relevant to the industrial practice (gas phase operation) since pentane and hexane isomers are non-permanent gases. Ideally, in light of the current TIP processes, the alkane isomer separation should be performed at or near the isomerisation temperature, i.e., above 373 K (see Fig 1.1, *Chapter 1*);

2) HRON and LRON separation: the separation of alkane isomers according to the degree of branching is commonly attributed to gasoline upgrading. Indeed, considering pentanes or hexanes separately, the most branched molecules are targeted. However, caution should be

taken in order to highlight the materials' performance under the simultaneous use of both classes. In the ideal scenario, the mono-branched iC5 must be present in the HRON fraction with the di-branched hexanes 23DMB and 22DMB to guarantee the maximum RON gain and not with the fraction of mono-branched hexanes (2MP/3MP) as performed by the MOFs $\text{Fe}_2(\text{BDP})_3$ and ZIF-77;

3) Cost: Most synthesised MOFs for separation are only obtained in the laboratory to assess their properties and comprehensively understand their adsorption behaviour. Researchers do not typically focus on optimising energy use, chemical toxicity, and synthesis processes. Although optimum separation performance can be obtained, the relative complexity associated with some organic linkers (nIm - ZIF-77, tcpb - $\text{Ca}(\text{H}_2\text{tcpb})$, H_3bttotb - Al-bttotb) would make the MOF scale-up synthesis difficult/expensive, which may become a major hindrance to the forward progression for industrial applications. Thus, reliance on inexpensive, structurally simple, and commercially available linkers is advantageous for economically favourable manufacturing. Bio-sourced or biomass-derived linkers are even more attractive since they exhibit minimal environmental impact;

4) Shaping and scale-up: The current performance evaluation of MOF materials is performed in their powdered state obtained from the small laboratory (mg scale) synthesis. However, the shaping process is indispensable to achieving ultimate industrial implementation, where the powder is structured into specific morphologies (agglomerates, beads, pellets, monoliths, etc.) to enhance mechanical strength and mass transfer as well as to reduce the pressure drop across the adsorber. Since the compatibility between the porous materials and binder agents directly affects the separation performance of the shaped material, research into the optimisation of binders and shaping processes should be devoted. Moreover, high-yielding production (g to kg) via relatively simple processes under mild conditions, minimising or without the use of non-hazardous solvents, is greatly desired. In brief: the “green” synthesis;

5) Development of adsorbents grading combination technology: the efficient cut of complex mixtures comprising all pentane and hexane isomers into HRON and LRON fractions is a challenging task that is very difficult to achieve with only one MOF. Therefore, loading more than one material with different separation functions into the same fixed bed might be an attractive option, in which their synergistic effect would mitigate the drawbacks of the individual components and enhance separation performance.

MOFs have exhibited an enormous potential to improve the overall effectiveness of TIP processes. Considering the rapid growth in this domain, we believe that new MOFs and synthesis processes will be developed to cope with the considerations above, and such configuration for splitting HRON and LRON molecules under relevant industrial conditions will materialise. Thus, we are optimistic that a TIP process filled with a MOF-based adsorption unit may be realised in the near future.

2.4 References

- (1) Moghadam, P. Z.; Li, A.; Wiggin, S. B.; Tao, A.; Maloney, A. G. P.; Wood, P. A.; Ward, S. C.; Fairen-Jimenez, D. Development of a Cambridge Structural Database Subset: A Collection of Metal-Organic Frameworks for Past, Present, and Future. *Chem. Mater.* **2017**, *29*, 2618–2625.
- (2) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705–714.
- (3) Rowsell, J. L. C.; Yaghi, O. M. Metal-Organic Frameworks: A New Class of Porous Materials. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.
- (4) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.
- (5) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (6) Tranchemontagne, D. J.; Tranchemontagne, J. L.; O’keeffe, M.; Yaghi, O. M. Secondary Building Units, Nets and Bonding in the Chemistry of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1257–1283.
- (7) Lu, W.; Wei, Z.; Gu, Z. Y.; Liu, T. F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T.; Bosch, M.; Zhou, H. C. Tuning the Structure and Function of Metal-Organic Frameworks via Linker Design. *Chem. Soc. Rev.* **2014**, *43*, 5561–5593.
- (8) Schoedel, A.; Li, M.; Li, D.; O’Keeffe, M.; Yaghi, O. M. Structures of Metal-Organic

- Frameworks with Rod Secondary Building Units. *Chem. Rev.* **2016**, *116*, 12466–12535.
- (9) Lin, R. B.; Xiang, S.; Zhou, W.; Chen, B. Microporous Metal-Organic Framework Materials for Gas Separation. *Chem* **2020**, *6*, 337–363.
- (10) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isorecticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469–472.
- (11) Surblé, S.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Férey, G. A New Isorecticular Class of Metal-Organic-Frameworks with the MIL-88 Topology. *Chem. Commun.* **2006**, 284–286.
- (12) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.
- (13) Deng, H.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gándara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; Kazumori, H.; O’Keeffe, M.; Terasaki, O.; Stoddart, J. F.; Yaghi, O. M. Large-Pore Apertures in a Series of Metal-Organic Frameworks. *Science* **2012**, *336*, 1018–1023.
- (14) Zhang, Y. B.; Zhou, H. L.; Lin, R. B.; Zhang, C.; Lin, J. Bin; Zhang, J. P.; Chen, X. M. Geometry Analysis and Systematic Synthesis of Highly Porous Isorecticular Frameworks with a Unique Topology. *Nat. Commun.* **2012**, *3*, 642.
- (15) Guillerm, V.; Ragon, F.; Dan-Hardi, M.; Devic, T.; Vishnuvarthan, M.; Campo, B.; Vimont, A.; Clet, G.; Yang, Q.; Maurin, G.; Férey, G.; Vittadini, A.; Gross, S.; Serre, C. A Series of Isorecticular, Highly Stable, Porous Zirconium Oxide Based Metal-Organic Frameworks. *Angew. Chemie - Int. Ed.* **2012**, *51*, 9267–9271.
- (16) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. High H₂ Adsorption in a Microporous Metal-Organic Framework with Open Metal Sites. *Angew. Chemie - Int. Ed.* **2005**, *44*, 4745–4749.
- (17) Lin, X.; Telepeni, I.; Blake, A. J.; Dailly, A.; Brown, C. M.; Simmons, J. M.; Zoppi, M.; Walker, G. S.; Thomas, K. M.; Mays, T. J.; Hubberstey, P.; Champness, N. R.; Schröder, M. High Capacity Hydrogen Adsorption in Cu(II) Tetracarboxylate Framework

- Materials: The Role of Pore Size, Ligand Functionalization, and Exposed Metal Sites. *J. Am. Chem. Soc.* **2009**, *131*, 2159–2171.
- (18) Li, B.; Wen, H. M.; Wang, H.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou, W.; Chen, B. A Porous Metal-Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity. *J. Am. Chem. Soc.* **2014**, *136*, 6207–6210.
- (19) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II) Coordination Sites. *Science*. **2012**, *335*, 1606–1610.
- (20) Li, L.; Lin, R. B.; Krishna, R.; Li, H.; Xiang, S.; Wu, H.; Li, J.; Zhou, W.; Chen, B. Ethane/Ethylene Separation in a Metal-Organic Framework with Iron-Peroxo Sites. *Science* **2018**, *362*, 443–446.
- (21) Xiang, S.; Zhou, W.; Liu, Y.; Chen, B. Exceptionally High Acetylene Uptake in a Microporous Metal-Organic Framework with Open Metal Sites. *ACS Natl. Meet. B. Abstr.* **2009**, *131*, 12415–12419.
- (22) Xiang, S.; Zhou, W.; Zhang, Z.; Green, M. A.; Liu, Y.; Chen, B. Open Metal Sites within Isostructural Metal-Organic Frameworks for Differential Recognition of Acetylene and Extraordinarily High Acetylene Storage Capacity at Room Temperature. *Angew. Chemie - Int. Ed.* **2010**, *49*, 4615–4618.
- (23) Moreau, F.; Da Silva, I.; Al Smail, N. H.; Easun, T. L.; Savage, M.; Godfrey, H. G. W.; Parker, S. F.; Manuel, P.; Yang, S.; Schröder, M. Unravelling Exceptional Acetylene and Carbon Dioxide Adsorption within a Tetra-Amide Functionalized Metal-Organic Framework. *Nat. Commun.* **2017**, *8*, 14085.
- (24) Lee, W. R.; Hwang, S. Y.; Ryu, D. W.; Lim, K. S.; Han, S. S.; Moon, D.; Choi, J.; Hong, C. S. Diamine-Functionalized Metal-Organic Framework: Exceptionally High CO₂ Capacities from Ambient Air and Flue Gas, Ultrafast CO₂ Uptake Rate, and Adsorption Mechanism. *Energy Environ. Sci.* **2014**, *7*, 744–751.
- (25) Kim, E. J.; Siegelman, R. L.; Jiang, H. Z. H.; Forse, A. C.; Lee, J. H.; Martell, J. D.; Milner, P. J.; Falkowski, J. M.; Neaton, J. B.; Reimer, J. A.; Weston, S. C.; Long, J. R. Cooperative Carbon Capture and Steam Regeneration with Tetraamine-Appended Metal-Organic Frameworks. *Science* **2020**, *369*, 392–396.

- (26) Ma, S.; Sun, D.; Wang, X. Sen; Zhou, H. C. A Mesh-Adjustable Molecular Sieve for General Use in Gas Separation. *Angew. Chemie - Int. Ed.* **2007**, *46*, 2458–2462.
- (27) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; Llewellyn, P. L.; Masciocchi, N.; Long, J. R. Methane Storage in Flexible Metal-Organic Frameworks with Intrinsic Thermal Management. *Nature* **2015**, *527*, 357–361.
- (28) Nakagawa, K.; Tanaka, D.; Horike, S.; Shimomura, S.; Higuchi, M.; Kitagawa, S. Enhanced Selectivity of CO₂ from a Ternary Gas Mixture in an Interdigitated Porous Framework. *Chem. Commun.* **2010**, *46*, 4258–4260.
- (29) Foo, M. L.; Matsuda, R.; Hijikata, Y.; Krishna, R.; Sato, H.; Horike, S.; Hori, A.; Duan, J.; Sato, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. An Adsorbate Discriminatory Gate Effect in a Flexible Porous Coordination Polymer for Selective Adsorption of CO₂ over C₂H₂. *J. Am. Chem. Soc.* **2016**, *138*, 3022–3030.
- (30) Dong, Q.; Zhang, X.; Liu, S.; Lin, R. B.; Guo, Y.; Ma, Y.; Yonezu, A.; Krishna, R.; Liu, G.; Duan, J.; Matsuda, R.; Jin, W.; Chen, B. Tuning Gate-Opening of a Flexible Metal–Organic Framework for Ternary Gas Sieving Separation. *Angew. Chemie - Int. Ed.* **2020**, *59*, 22756–22762.
- (31) Wang, J.; Zhang, Y.; Zhang, P.; Hu, J.; Lin, R. B.; Deng, Q.; Zeng, Z.; Xing, H.; Deng, S.; Chen, B. Optimizing Pore Space for Flexible-Robust Metal-Organic Framework to Boost Trace Acetylene Removal. *J. Am. Chem. Soc.* **2020**, *142*, 9744–9751.
- (32) Wang, X.; Krishna, R.; Li, L.; Wang, B.; He, T.; Zhang, Y. Z.; Li, J. R.; Li, J. Guest-Dependent Pressure Induced Gate-Opening Effect Enables Effective Separation of Propene and Propane in a Flexible MOF. *Chem. Eng. J.* **2018**, *346*, 489–496.
- (33) Yang, L.; Cui, X.; Zhang, Y.; Yang, Q.; Xing, H. A Highly Sensitive Flexible Metal-Organic Framework Sets a New Benchmark for Separating Propyne from Propylene. *J. Mater. Chem. A* **2018**, *6*, 24452–24458.
- (34) Zhang, Z.; Yang, Q.; Cui, X.; Yang, L.; Bao, Z.; Ren, Q.; Xing, H. Sorting of C₄ Olefins with Interpenetrated Hybrid Ultramicroporous Materials by Combining Molecular Recognition and Size-Sieving. *Angew. Chemie - Int. Ed.* **2017**, *56*, 16282–16287.

- (35) Herm, Z. R.; Bloch, E. D.; Long, J. R. Hydrocarbon Separations in Metal-Organic Frameworks. *Chem. Mater.* **2014**, *26*, 323–338.
- (36) Bao, Z.; Chang, G.; Xing, H.; Krishna, R.; Ren, Q.; Chen, B. Potential of Microporous Metal-Organic Frameworks for Separation of Hydrocarbon Mixtures. *Energy Environ. Sci.* **2016**, *9*, 3612–3641.
- (37) Gehre, M.; Guo, Z.; Rothenberg, G.; Tanase, S. Sustainable Separations of C4-Hydrocarbons by Using Microporous Materials. *ChemSusChem* **2017**, *10*, 3947–3963.
- (38) Barnett, B. R.; Gonzalez, M. I.; Long, J. R. Recent Progress Towards Light Hydrocarbon Separations Using Metal–Organic Frameworks. *Trends Chem.* **2019**, *1*, 159–171.
- (39) Pei, J.; Shao, K.; Zhang, L.; Wen, H. M.; Li, B.; Qian, G. Current Status of Microporous Metal–Organic Frameworks for Hydrocarbon Separations. *Top. Curr. Chem.* **2019**, 377.
- (40) Li, H.; Li, L.; Lin, R.-B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B. Porous Metal-Organic Frameworks for Gas Storage and Separation: Status and Challenges. *EnergyChem* **2019**, *1*, 100006.
- (41) Cui, W. G.; Hu, T. L.; Bu, X. H. Metal–Organic Framework Materials for the Separation and Purification of Light Hydrocarbons. *Adv. Mater.* **2020**, *32*, 1806445.
- (42) Mukherjee, S.; Sensharma, D.; Qazvini, O. T.; Dutta, S.; Macreadie, L. K.; Ghosh, S. K.; Babarao, R. Advances in Adsorptive Separation of Benzene and Cyclohexane by Metal-Organic Framework Adsorbents. *Coord. Chem. Rev.* **2021**, *437*, 213852.
- (43) Fu, M.; Wang, Y.; Wang, X.; Sun, D. Metal-Organic Framework Materials for Light Hydrocarbon Separation. *Chempluschem* **2021**, *86*, 387–395.
- (44) Zhang, Z.; Peh, S. B.; Kang, C.; Chai, K.; Zhao, D. Metal-Organic Frameworks for C6–C8 Hydrocarbon Separations. *EnergyChem* **2021**, *3*, 100057.
- (45) Yang, R. T. *Adsorbents: Fundamentals and Applications*; John Wiley & Sons, 2003.
- (46) Adil, K.; Belmabkhout, Y.; Pillai, R. S.; Cadiau, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Gas/Vapour Separation Using Ultra-Microporous Metal-Organic Frameworks: Insights into the Structure/Separation Relationship. *Chem. Soc. Rev.* **2017**, *46*, 3402–3430.

- (47) Lin, R. B.; Xiang, S.; Xing, H.; Zhou, W.; Chen, B. Exploration of Porous Metal–Organic Frameworks for Gas Separation and Purification. *Coord. Chem. Rev.* **2019**, *378*, 87–103.
- (48) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A Microporous Metal–Organic Framework for Gas-Chromatographic Separation of Alkanes. *Angew. Chemie - Int. Ed.* **2006**, *45*, 1390–1393.
- (49) Bárcia, P. S.; Zapata, F.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. Kinetic Separation of Hexane Isomers by Fixed-Bed Adsorption with a Microporous Metal - Organic Framework. *J. Phys. Chem. B* **2007**, *111*, 6101–6103.
- (50) Dubbeldam, D.; Galvin, C. J.; Walton, K. S.; Ellis, D. E.; Snurr, R. Q. Separation and Molecular-Level Segregation of Complex Alkane Mixtures in Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2008**, 10884–10885.
- (51) Ling, Y.; Chen, Z. X.; Zhai, F. P.; Zhou, Y. M.; Weng, L. H.; Zhao, D. Y. A Zinc(II) Metal–Organic Framework Based on Triazole and Dicarboxylate Ligands for Selective Adsorption of Hexane Isomers. *Chem. Commun.* **2011**, *47*, 7197–7199.
- (52) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal–Organic Framework with Triangular Channels. *Science* **2013**, *340*, 960–964.
- (53) Wang, D.; Dong, X.; Han, Y.; Liu, Y. Separation of Hexane Isomers by Introducing “Triangular-like and Quadrilateral-like Channels” in a Bcu-Type Metal–Organic Framework. *Nano Res.* **2021**, *14*, 526–531.
- (54) Chung, Y. G.; Bai, P.; Haranczyk, M.; Leperi, K. T.; Li, P.; Zhang, H.; Wang, T. C.; Duerinck, T.; You, F.; Hupp, J. T.; Farha, O. K.; Siepmann, J. I.; Snurr, R. Q. Computational Screening of Nanoporous Materials for Hexane and Heptane Isomer Separation. *Chem. Mater.* **2017**, *29*, 6315–6328.
- (55) Peng, L.; Zhu, Q.; Wu, P.; Wu, X.; Cai, W. High-Throughput Computational Screening of Metal–Organic Frameworks with Topological Diversity for Hexane Isomer Separations. *Phys. Chem. Chem. Phys.* **2019**, *21*, 8508–8516.
- (56) Solanki, V. A.; Borah, B. Ranking of Metal–Organic Frameworks (MOFs) for Separation

- of Hexane Isomers by Selective Adsorption. *Ind. Eng. Chem. Res.* **2019**, *58*, 20047–20065.
- (57) Solanki, V. A.; Borah, B. Exploring the Potentials of Metal-Organic Frameworks as Adsorbents and Membranes for Separation of Hexane Isomers. *J. Phys. Chem. C* **2019**, *123*, 17808–17822.
- (58) Solanki, V. A.; Borah, B. High-Throughput Computational Screening of 12,351 Real Metal-Organic Framework Structures for Separation of Hexane Isomers: A Quest for a Yet Better Adsorbent. *J. Phys. Chem. C* **2020**, *124*, 4582–4594.
- (59) Denayer, J. F. M.; Ocakoglu, R. A.; Arik, I. C.; Kirschhock, C. E. A.; Martens, J. A.; Baron, G. V. Rotational Entropy Driven Separation of Alkane/Isoalkane Mixtures in Zeolite Cages. *Angew. Chemie - Int. Ed.* **2005**, *44*, 400–403.
- (60) Denayer, J. F. M.; Ocakoglu, A. R.; Martens, J. A.; Baron, G. V. Investigation of Inverse Shape Selectivity in Alkane Adsorption on SAPO-5 Zeolite Using the Tracer Chromatography Technique. *J. Catal.* **2004**, *226*, 240–244.
- (61) Denayer, J. F. M.; Ocakoglu, R. A.; Thybaut, J.; Marin, G.; Jacobs, P.; Martens, J.; Baron, G. V. N- and Isoalkane Adsorption Mechanisms on Zeolite MCM-22. *J. Phys. Chem. B* **2006**, *110*, 8551–8558.
- (62) Bárcia, P. S.; Guimarães, D.; Mendes, P. A. P.; Silva, J. A. C.; Guillerm, V.; Chevreau, H.; Serre, C.; Rodrigues, A. E. Reverse Shape Selectivity in the Adsorption of Hexane and Xylene Isomers in MOF UiO-66. *Microporous Mesoporous Mater.* **2011**, *139*, 67–73.
- (63) Chang, N.; Yan, X. P. Exploring Reverse Shape Selectivity and Molecular Sieving Effect of Metal-Organic Framework UiO-66 Coated Capillary Column for Gas Chromatographic Separation. *J. Chromatogr. A* **2012**, *1257*, 116–124.
- (64) Ramsahye, N. A.; Trens, P.; Shepherd, C.; Gonzalez, P.; Trung, T. K.; Ragon, F.; Serre, C. The Effect of Pore Shape on Hydrocarbon Selectivity on UiO-66(Zr), HKUST-1 and MIL-125(Ti) Metal Organic Frameworks: Insights from Molecular Simulations and Chromatography. *Microporous Mesoporous Mater.* **2014**, *189*, 222–231.
- (65) Duerinck, T.; Denayer, J. F. M. Unusual Chain Length Dependent Adsorption of Linear

- and Branched Alkanes on UiO-66. *Adsorption* **2014**, *20*, 251–259.
- (66) Cuadrado-Collados, C.; Rojas-Mayorga, C. K.; Saavedra, B.; Martinez-Escandell, M.; Osiński, J. M.; Moghadam, P. Z.; Fairen-Jimenez, D.; Silvestre-Albero, J. Reverse Hierarchy of Alkane Adsorption in Metal-Organic Frameworks (MOFs) Revealed by Immersion Calorimetry. *J. Phys. Chem. C* **2019**, *123*, 11699–11706.
- (67) Dubbeldam, D.; Krishna, R.; Calero, S.; Yazaydin, A. Ö. Computer-Assisted Screening of Ordered Crystalline Nanoporous Adsorbents for Separation of Alkane Isomers. *Angew. Chemie - Int. Ed.* **2012**, *51*, 11867–11871.
- (68) Mendes, P. A. P.; Ragon, F.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Hexane Isomers Sorption on a Functionalized Metal-Organic Framework. *Microporous Mesoporous Mater.* **2013**, *170*, 251–258.
- (69) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. Separation of C6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A. *Ind. Eng. Chem. Res.* **2012**, *51*, 4692–4702.
- (70) Bury, W.; Walczak, A. M.; Leszczyński, M. K.; Navarro, J. A. R. Rational Design of Noncovalent Diamondoid Microporous Materials for Low-Energy Separation of C6-Hydrocarbons. *J. Am. Chem. Soc.* **2018**, *140*, 15031–15037.
- (71) Suh, B. L.; Kim, J. Reverse Shape Selectivity of Hexane Isomer in Ligand Inserted MOF-74. *RSC Adv.* **2020**, *10*, 22601–22605.
- (72) Chen, B.; Yang, Z.; Zhu, Y.; Xia, Y. Zeolitic Imidazolate Framework Materials: Recent Progress in Synthesis and Applications. *J. Mater. Chem. A* **2014**, *2*, 16811–16831.
- (73) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O’Keeffe, M.; Yaghi, O. M. Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186–10191.
- (74) Chang, N.; Gu, Z. Y.; Yan, X. P. Zeolitic Imidazolate Framework-8 Nanocrystal Coated Capillary for Molecular Sieving of Branched Alkanes From Linear Alkanes along with High-Resolution Chromatographic Separation of Linear Alkanes. *J. Am. Chem. Soc.* **2010**, *132*, 13645–13647.
- (75) Luebbers, M. T.; Wu, T.; Shen, L.; Masel, R. I. Effects of Molecular Sieving and

- Electrostatic Enhancement in the Adsorption of Organic Compounds on the Zeolitic Imidazolate Framework ZIF-8. *Langmuir* **2010**, *8*, 15625–15633.
- (76) Mendes, P. A. P.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Single and Multicomponent Adsorption of Hexane Isomers in the Microporous ZIF-8. *Microporous Mesoporous Mater.* **2014**, *194*, 146–156.
- (77) Zhang, L.; Qian, G.; Liu, Z.; Cui, Q.; Wang, H.; Yao, H. Adsorption and Separation Properties of N-Pentane/Isopentane on ZIF-8. *Sep. Purif. Technol.* **2015**, *156*, 472–479.
- (78) Ferreira, A. F. P.; Mittelmeijer-Hazeleger, M. C.; Granato, M. A.; Martins, V. F. D.; Rodrigues, A. E.; Rothenberg, G. Sieving Di-Branched from Mono-Branched and Linear Alkanes Using ZIF-8: Experimental Proof and Theoretical Explanation. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8795–8804.
- (79) Zhang, K.; Lively, R. P.; Zhang, C.; Chance, R. R.; Koros, W. J.; Sholl, D. S.; Nair, S. Exploring the Framework Hydrophobicity and Flexibility of ZIF-8: From Biofuel Recovery to Hydrocarbon Separations. *J. Phys. Chem. Lett.* **2013**, *4*, 3618–3622.
- (80) Mendes, P. A. P.; Horcajada, P.; Rives, S.; Ren, H.; Rodrigues, A. E.; Devic, T.; Magnier, E.; Trens, P.; Jolic, H.; Ollivier, J.; Maurin, G.; Serre, C.; Silva, J. A. C. A Complete Separation of Hexane Isomers by a Functionalized Flexible Metal Organic Framework. *Adv. Funct. Mater.* **2014**, *24*, 7666–7673.
- (81) Lv, D.; Wang, H.; Chen, Y.; Xu, F.; Shi, R.; Liu, Z.; Wang, X.; Teat, S. J.; Xia, Q.; Li, Z.; Li, J. Iron-Based Metal-Organic Framework with Hydrophobic Quadrilateral Channels for Highly Selective Separation of Hexane Isomers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 6031–6038.
- (82) Mendes, P.; Rodrigues, A.; Horcajada, P.; Eubank, J.; Devic, T.; Serre, C.; Silva, J. Separation of Hexane Isomers on Rigid Porous Metal Carboxylate-Based Metal-Organic Frameworks. *Adsorpt. Sci. Technol.* **2014**, *32*, 475–488.
- (83) Assen, A. H.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Xue, D. X.; Jiang, H.; Eddaoudi, M. Ultra-Tuning of the Rare-Earth Fcu-MOF Aperture Size for Selective Molecular Exclusion of Branched Paraffins. *Angew. Chemie - Int. Ed.* **2015**, *54*, 14353–14358.
- (84) Li, X.; Wang, H.; Zou, J.; Li, J. Metal–Organic Frameworks with Ftw-Type

- Connectivity: Design, Pore Structure Engineering, and Potential Applications. *CrystEngComm* **2022**, *24*, 2189–2200.
- (85) Wang, H.; Dong, X.; Lin, J.; Teat, S. J.; Jensen, S.; Cure, J.; Alexandrov, E. V.; Xia, Q.; Tan, K.; Wang, Q.; Olson, D. H.; Proserpio, D. M.; Chabal, Y. J.; Thonhauser, T.; Sun, J.; Han, Y.; Li, J. Topologically Guided Tuning of Zr-MOF Pore Structures for Highly Selective Separation of C6 Alkane Isomers. *Nat. Commun.* **2018**, *9*, 1745.
- (86) Wang, H.; Dong, X.; Velasco, E.; Olson, D. H.; Han, Y.; Li, J. One-of-a-Kind: A Microporous Metal-Organic Framework Capable of Adsorptive Separation of Linear, Mono- and Di-Branched Alkane Isomers via Temperature- and Adsorbate-Dependent Molecular Sieving. *Energy Environ. Sci.* **2018**, *11*, 1226–1231.
- (87) Yu, L.; Dong, X.; Gong, Q.; Acharya, S. R.; Lin, Y.; Wang, H.; Han, Y.; Thonhauser, T.; Li, J. Splitting Mono- and Dibranched Alkane Isomers by a Robust Aluminum-Based Metal-Organic Framework Material with Optimal Pore Dimensions. *J. Am. Chem. Soc.* **2020**, *142*, 6925–6929.
- (88) Wang, H.; Dong, X.; Ding, J.; Wang, K.; Yu, L.; Zhang, S.; Han, Y.; Gong, Q.; Ma, A.; Li, J. Upgrading Octane Number of Naphtha by a Robust and Easily Attainable Metal-Organic Framework through Selective Molecular Sieving of Alkane Isomers. *Chem. - A Eur. J.* **2021**, *27*, 11795–11798.
- (89) Ji, Z.; Wang, H.; Canossa, S.; Wuttke, S.; Yaghi, O. M. Pore Chemistry of Metal–Organic Frameworks. *Adv. Funct. Mater.* **2020**, *30*, 2000238.
- (90) Yu, Q.; Guo, L.; Lai, D.; Zhang, Z.; Yang, Q.; Yang, Y.; Ren, Q.; Bao, Z. A Pore-Engineered Metal-Organic Framework with Mixed Ligands Enabling Highly Efficient Separation of Hexane Isomers for Gasoline Upgrading. *Sep. Purif. Technol.* **2021**, *268*, 118646.

3 FIXED BED ADSORPTION: EXPERIMENTAL, MODELLING, AND NUMERICAL SIMULATION

This chapter describes the development of a new chromatographic-based fixed bed adsorption apparatus to measure breakthrough curves of non-permanent gas alkane feeds, fundamental for screening new adsorbent materials for their separation into HRON and LRON fractions. The experimental apparatus especially built for the measurement of single and multicomponent breakthrough curves of pentane and hexane isomers is shown together with the procedure to set up/study the adsorption equilibrium, kinetics and the dynamics of the fixed bed. The system operates in a wide range of working conditions that are representative of current TIP processes, including the capability to study the adsorption of complex septenary mixtures. Also, a two-step small-scale laboratory PSA unit was developed and coupled to the breakthrough apparatus for the preliminary evaluation of the cyclic operation of a few grams of adsorbents.

Thereafter, emphasis is given to the analysis of the experimental data, referring to the adsorption equilibrium models used for their correlation and interpretation. Three different isotherm models are considered: Langmuir, Dual-site Langmuir (DSL), and Sips. Finally, a general fixed bed adsorption mathematical model was developed based on the fundamental material and energy conservation laws, including axial dispersion coupled with thermodynamic relations and a lumped kinetic linear mass transfer rate model. The numerical package is intended to qualitatively and quantitative simulate the observed transient adsorption behaviour of the pentane and hexane isomers in the column, helping validate the thermodynamic and kinetic parameters that conveniently describe their overall dynamics. The mathematical model is also fundamental for the preliminary design of cyclic adsorption operation using the new screened adsorbents.

3.1 Introduction

In most commercial adsorption-based separation processes, the adsorbent is in contact with a fluid in a fixed bed adsorber.¹ The fluid flows through the packed bed while the adsorbent particles are held fixed in position. Invariably, these adsorbers operate in a transient mode, meaning that the compositions of guest molecules in the fluid phase and within the adsorbent (solid phase) vary with bed position and time. Such operation mode gives rise to several phenomena observed in the so-called breakthrough curves, which are directly related to the efficiency of the process and later important for the scale-up to an industrial level.^{2,3} Therefore, a good understanding of adsorption equilibria, kinetics, and dynamics of such systems is required for rational process design and optimization.⁴

Experimental data on the transient breakthrough of mixtures across fixed bed adsorbers are generally used to assess the separation performance of a given porous adsorbent. Breakthrough curves describe the effluent concentration-time history and are probably the best way to evaluate the efficiency of a material, as they reflect a more realistic combined influence of adsorption selectivity and adsorption capacity.^{5,6} Furthermore, they can be influenced by axial dispersion, adsorption equilibrium, and kinetic effects (mass transfer rates from bulk fluid phase to interior of the adsorbent).² Thus, to establish the extent of the relative importance of these mechanisms in determining the separation performance of an adsorbent material, numerical breakthrough simulations are usually performed and compared with experimental data.⁷ Moreover, breakthrough curve prediction through mathematical models is a valuable tool for design and optimization purposes.

This chapter is divided into five main sections: Section 3.2 fully describes the new experimental system developed to conduct screening studies on different adsorbents to assess their ability to fractionate pentane and hexane isomers in a fixed bed column. Section 3.3 introduces the metrics used to quantify the adsorbent separation performance, such as the average RON value of the mixture at the column outlet, ideal adsorption productivity, and adsorption selectivity. Section 3.4 highlights a few adsorption isotherm models used to interpret and correlate the measured experimental data. Section 3.5 presents the mathematical model developed to simulate the experimental transient breakthrough curves. The numerical procedure applied for solving the fundamental differential/algebraic equations is also shown. Finally, section 3.6 highlights concluding remarks.

3.2 Experimental Setup for Measuring Gas Adsorption Equilibrium

As a fundamental part of this research, a new fixed bed adsorption apparatus was designed and built to evaluate different microporous materials regarding their ability to adsorb and fractionate pentanes and hexanes isomers into HRON and LRON fractions. The also called screening apparatus was developed to measure breakthrough curves covering a range of working conditions (temperature and hydrocarbon pressures) relevant to the industrial separation. Moreover, it is imperative to highlight that the system allows working with complex multicomponent mixtures, such as quinary mixtures of all hexane isomers and septenary mixtures of pentane and hexane isomers (rarely addressed in the literature). From these experiments, adsorption equilibrium isotherms were collected and the overall dynamics of the system recorded. At a further stage, after finishing the screening studies, the apparatus was upgraded to test the most promising screened adsorbent material under cyclic adsorption/desorption operation.

3.2.1 Experimental Apparatus for Screening Studies

The screening apparatus developed to measure single and multicomponent breakthrough curves of pentane and hexane isomers in the vapor phase is depicted in Figure 3.1 and mainly comprises the following devices: (1) two gas chromatographs (GC, YL 6500, YL Instruments Co., Ltd.), one being preparative and the other being analytic. They are equipped with different injectors (packed and capillary inlet), different detectors (thermal conductivity detector (TCD) and flame ionization detector (FID)), and with advanced pneumatic control (APC) systems to electronically regulate the gas flow rate; (2) two mass flow controllers (MFC1/MFC2, MC-5SCCM-D/5M, Alicat Scientific) peripheral devices were used for controlling the flow rates of the inert gas; (3) one syringe pump (SP, Legato® 100, KD Scientific) for continuously injecting the paraffins into the system; (4) adsorption columns (AC, 316 stainless steel, Swagelok) for packing the adsorbent material; (5) one capillary column (CC, Equity-1, Supelco) for analysing the effluent composition of the AC column; (6) three automatic valves (V1/V2/V3, VICI, Valco Instruments Co.) for switching and sampling the gases inside the system; (7) a manual valve (V4, SS-41GXS1, Swagelok) for switching the bypass line; (8) one temperature regulator (TR, ACS-13A, Shinko) for controlling external lines temperature;

and (9) a personal computer (PC, *HP ProBook 450 G3*, *HP Inc.*) for monitoring, data gathering, and automation of the overall experimental system.



Figure 3.1 | Real view of the screening apparatus developed to measure single and multicomponent breakthrough curves of pentane and hexane isomers: a) front view of the complete experimental unit; **a1)** internal view of the preparative GC, with visible switching valves (V1) and (V2), AC, streams, and inlet of the TCD; **a2)** internal view of the analytical GC, with visible sampling valve, the outlet of S/SP injector and inlet of the FID; **a3)** close-up of the SP and MFC's, and **a4)** close-up of CC.

Two different columns were used on the screening studies: 1) with a 0.1 m length and 0.0046 m internal diameter, and 2) with a 0.12 m length and 0.01 m internal diameter (shown in Figure 3.1 panel a1). The choice between them was based on the form of the adsorbent materials, such as powdered state, shaped beads, and structured monoliths, and also on the amount of adsorbent material available for study.

Figure 3.2 shows the schematic diagram of the screening apparatus, which consists of three main sections: (i) gas preparation, (ii) adsorption, and (iii) analytical section. In the gas preparation section, the carrier gas and the paraffins are introduced into the system. Helium (He) is used as a carrier gas due to its inertness and enters the system in four different streams: the lines (1), (2), make-up, and (8). The first three lines are directed to the preparative GC, and line (8) is sent to the analytical part. The lines (1) and (2) are controlled by the MFCs 1 e 2, respectively, while the make-up and line (8) pass through the APC system. The hydrocarbon stream in the liquid phase is continuously introduced with the SP in the He gas flowing in the line (1). Then, the mixture runs into the inner heating region of the packed inlet injector (vaporizer), located on the preparative GC, where the paraffins are completely vaporized.

The adsorption section consists of an AC entirely filled with the adsorbent material and operated inside a precise ventilated oven of the preparative GC, that assures practically isothermal temperature of the devices inside it. The mixture coming from the vaporizer and the pure He from line (2) runs to a switching 4-ports valve (V1) that allows the selection of which line will pass by the AC via line (5). The line that does not enter the AC is bypassed. The make-up line is used to dilute the effluent of the AC before entering the reference side of the TCD. The line that connects the preparative to the analytic GC, transfer line (TL), is thermally controlled to keep the temperature stable and avoid gas condensation.

In the last section, analytical, the AC effluent flowing in the TL and the pure He from the line (8) runs to a sampling 6-ports valve (V3), which has a loop of 0.25 mL connected. This valve operates cyclically, and in a pre-defined time, the pure He stream drags an aliquot of the effluent paraffin mixture to be chromatographically evaluated. The CC has a 15 m length, with 0.1 mm outside diameter and 0.1 μ m poly(dimethyl sulfoxane) coating, and is immersed in an ice-water bath for better separation of component peaks⁸. Before entering the CC, the aliquot passes through the capillary inlet injector (split/splitless, S/SP), which delivers only a small quantity of this sample for analysis. In the following, the effluent stream of the CC goes to the FID detector, and its composition is evaluated.

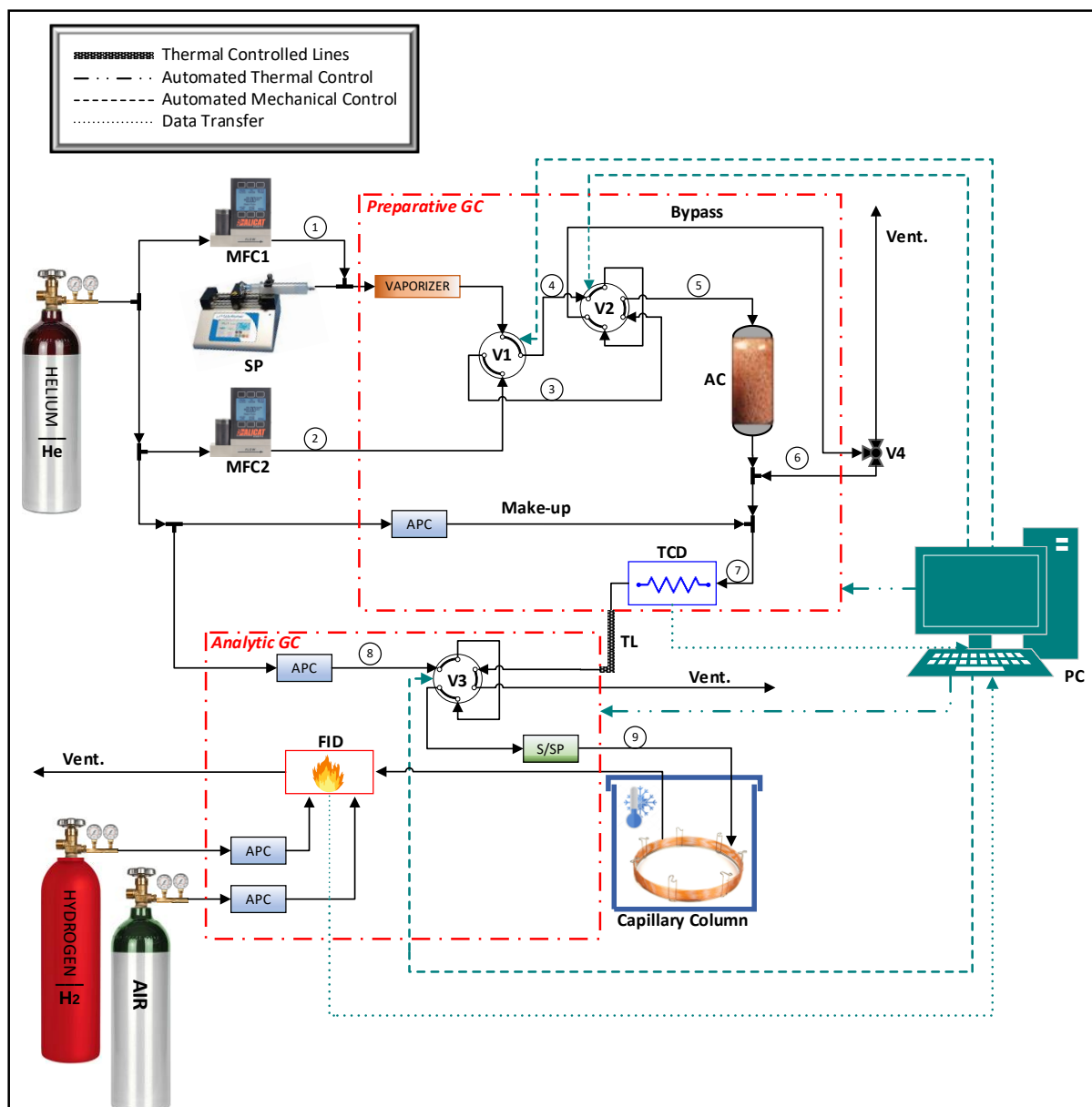


Figure 3.2 | Schematic diagram of the screening apparatus developed to measure single and multicomponent breakthrough curves.

* The analytical section is strictly necessary only for multicomponent experiments;

* The He streams corresponding to the reference side of TCD, make-up for the packed inlet injector and FID detector, and split flow for the capillary inlet injector (all controlled by the APC's modules) were omitted for clarity.

The system is entirely automated through a LabView software to sense and record the device's digital information and control the valves' position, as shown in Figure 3.3. The devices MFCs, SP, TR, and the valves (V1/V2/V3) are connected to a laboratory power supply (230V AC), which communicates with the PC via a USB control module, being their communication performed through a standard RS-232 serial protocol. The GC's components, such as oven

temperature, APC modules, injectors (packed and capillary inlet), and detectors (TCD/FID), are controlled using the YL-Clarity data acquisition software (YL Instruments Co., Ltd.).

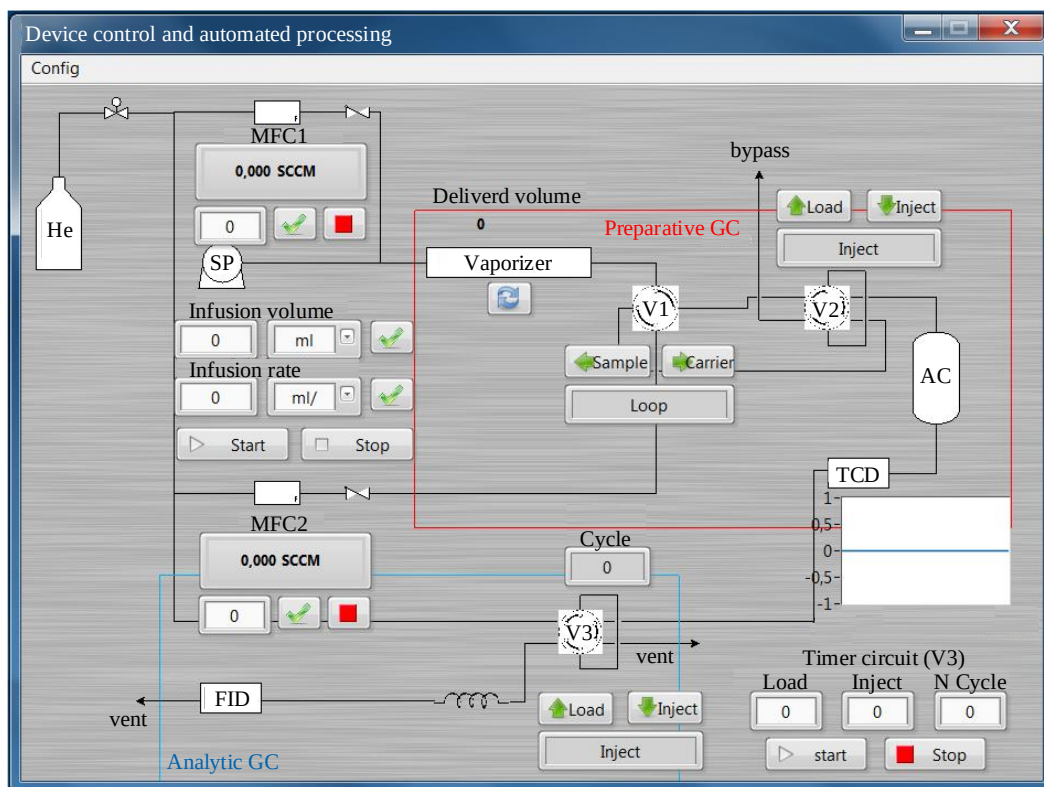


Figure 3.3 | Software interface for device control and automated processing.

All lines coming from the cylinders, which connect directly on the GC's entrance, and in the MFC's inlets, are in 1/8" of external diameter. From those points, they were reduced to 1/16" diameter.

3.2.1.1 Experimental Procedure to Measure Single Component Breakthrough Curves

The experimental procedure to obtain single component breakthrough curves consists of continuously measuring the concentration profile of the hydrocarbon species at the outlet of the AC as a function of time with the TCD. Therefore, the packed bed is operated by introducing, at the inlet, the feed containing the paraffin species diluted in He at a particular alkane partial pressure and temperature.

Before the time zero of an experiment, the switching valve (V1) directs pure He that flows through line (2) to the AC and bypasses the mixture (He + paraffin) that comes from the vaporizer (configuration shown in Figure 3.2). The column bypass is incorporated to check if

the vaporization of the paraffin is stable with a constant concentration signal in the TCD. Once the vaporization of the mixture reaches the equilibrium state, the experiment can be started. Then, the 3-way ball valve (V4) is directed to vent manually, and when the TCD reaches its inert baseline (pure He), the valve (V1) is actuated, allowing the mixture to run through the AC (time zero of the experiment). In the adsorption course, each adsorbent layer packed in the bed becomes loaded with the adsorbate species from the percolating gas as long as the state of equilibrium with the feed concentration is reached. This equilibration process proceeds gradually, layer by layer, from the inlet point to the outlet point of the column, as illustrated by Figure 3.4. When the front edge of the mass transfer zone approaches the outlet point of the column, the breakthrough curve occurs. The adsorbate concentration increases (TCD signal) due to its advancement, and once the entire mass transfer zone leaves the column, the bed is completely saturated to the equilibrium loading, and the adsorbate concentration at the outlet is equal to the inlet of the column.⁹

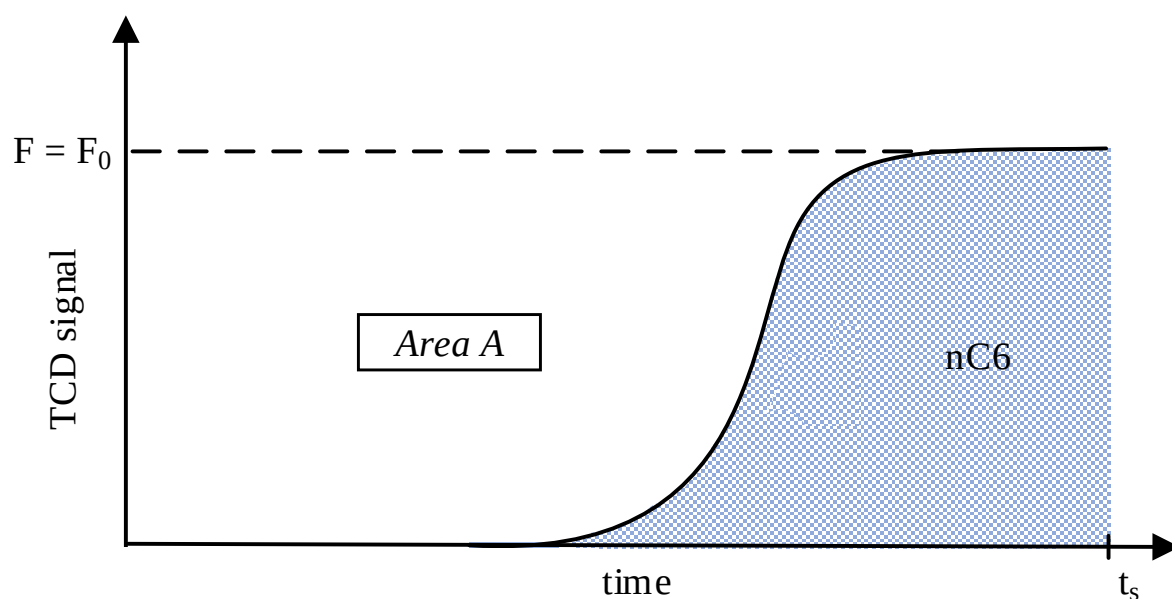


Figure 3.4 | Schematic representation of the experimental procedure for obtaining the typical single component breakthrough curve in a fixed bed adsorption process and calculating the loading.

When the saturation state is reached the experiment finishes, i.e., the paraffin injection by the SP is cut, and the valve (V1) is actuated again. Thus, the He gas flowing through line (2) performs the desorption of the packed column until the TCD approaches the inert baseline signal. After that, another run can be performed. One run means one equilibrium point of the adsorption equilibrium isotherm.

The number of moles retained in the packed bed at equilibrium conditions, q_{exp} ($mol.kg^{-1}$), often called as loading, is simply the *Area A*, shown in Figure 3.4, and can be calculated by integrating the molar history of the complete breakthrough curve, as follows:

$$q_{exp} = \frac{1}{m_s} \left(F_f t_s - \int_0^{t_s} F dt - \varepsilon_b V_{ac} C_f \right) \quad (3.1)$$

where m_s (kg) is the mass of adsorbent packed in the column, F_f and F ($mol.s^{-1}$) are the molar flow rate of adsorbate species at the feed inlet and outlet of the column, respectively, t_s (s) is the saturation time, ε_b is the porosity of the packed bed, V_{ac} (m^3) is the volume of the adsorption column, and C_f ($mol.m^{-3}$) is the feed gas concentration of the adsorbate species.

Through the subtraction of the total rectangle area ($F_f t_s$) to the area under the breakthrough curve calculated by ($\int_0^{t_s} F dt$) the adsorption *Area A* is obtained. The term $\varepsilon_b V_{ac} C_f / m_s$ represents the amount of adsorbate gas in the column void space. The area under the breakthrough curve was calculated using the trapezoidal rule shown in Eq. 3.2:

$$\int_0^{t_s} F dt = \sum_{i=0}^{t_s} \left(\frac{(F_{i+1} + F_i)(t_{i+1} - t_1)}{2} \right) \quad (3.2)$$

where i is the increment that determines the time position from 0 to t_s .

3.2.1.2 Experimental Procedure to Measure Multicomponent Breakthrough Curves

For experiments involving multicomponent mixtures, samples from the outlet point of the adsorption column are collected and chromatographically evaluated in real-time, as illustrated in Figure 3.5, for a typical quinary mixture of hexane isomers as an example.

When the experiment starts, the sampling valve (V3) is in the inject position (configuration shown in Figure 3.2), and only pure He from the line (8) passes through the loop and goes to the CC. Meanwhile, the column effluent is directed through the vent line. Shortly after, the valve (V3) is actuated, allowing the AC effluent to fill the loop (load position), before leaving the system. On the next actuation time of this valve, the He flow drags the sample aliquot inside the loop for analysis in the CC. This procedure repeats successively over the entire experiment until the AC reaches the saturation stage.

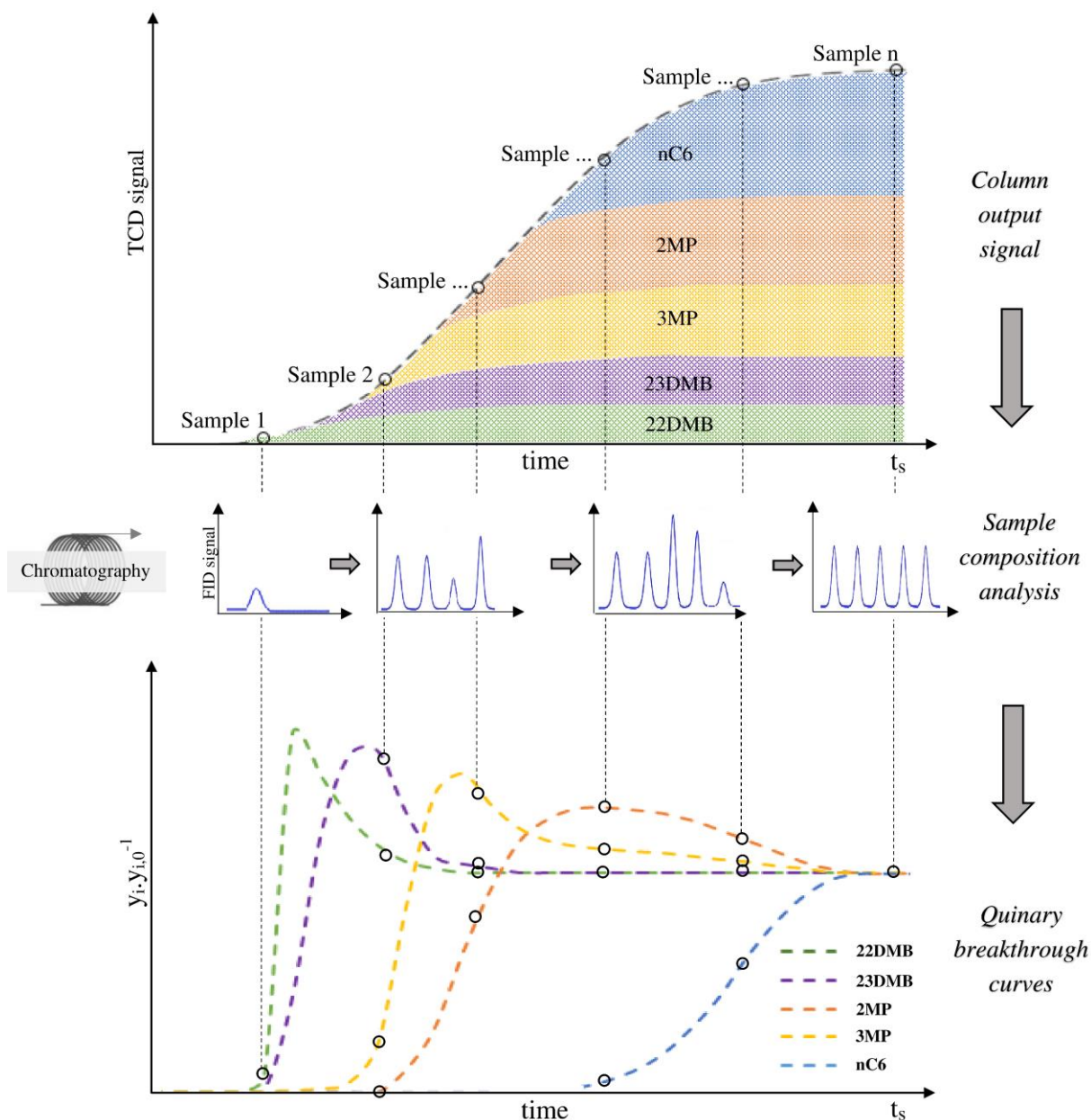


Figure 3.5 | Schematic representation of the experimental procedure for obtaining the typical multicomponent breakthrough curves in a fixed bed adsorption process (e.g., a mixture of hexane isomers).

Prior to the experiments, several calibration studies were performed to analyse the influence of gas flow rate and composition on the respective chromatographs measured by the analytical GC in the range of the experimental conditions covered through this work. Thus, the measured concentration multicomponent breakthrough curves are rebuilt to plot the molar fraction of each compound as a function of time for each sample evaluated (Figure 3.5).

For the adsorption of multicomponent mixtures, a concentration overshoot can be observed for the weaker adsorbable components as a typical result of thermodynamic

competition and displacement.¹⁰ As a result, a different breakthrough behaviour is observed compared to single component adsorption. In this case, to calculate the equilibrium loading, the overshoot area should be discounted from the breakthrough curve, as shown in Figure 3.6. In graphical terms, the loading for the first isomer to elute from AC, in this example 22DMB, is equal to area *A* minus the overshoot area *OS(A)*. For the second isomer, 23DMB, the loading is equal to area *A* plus area *B* minus roll-up *OS(B)* and so on for the other isomers. However, Eq. 3.1 is still valid for evaluating the individual loading of each compound in multicomponent breakthrough curves.

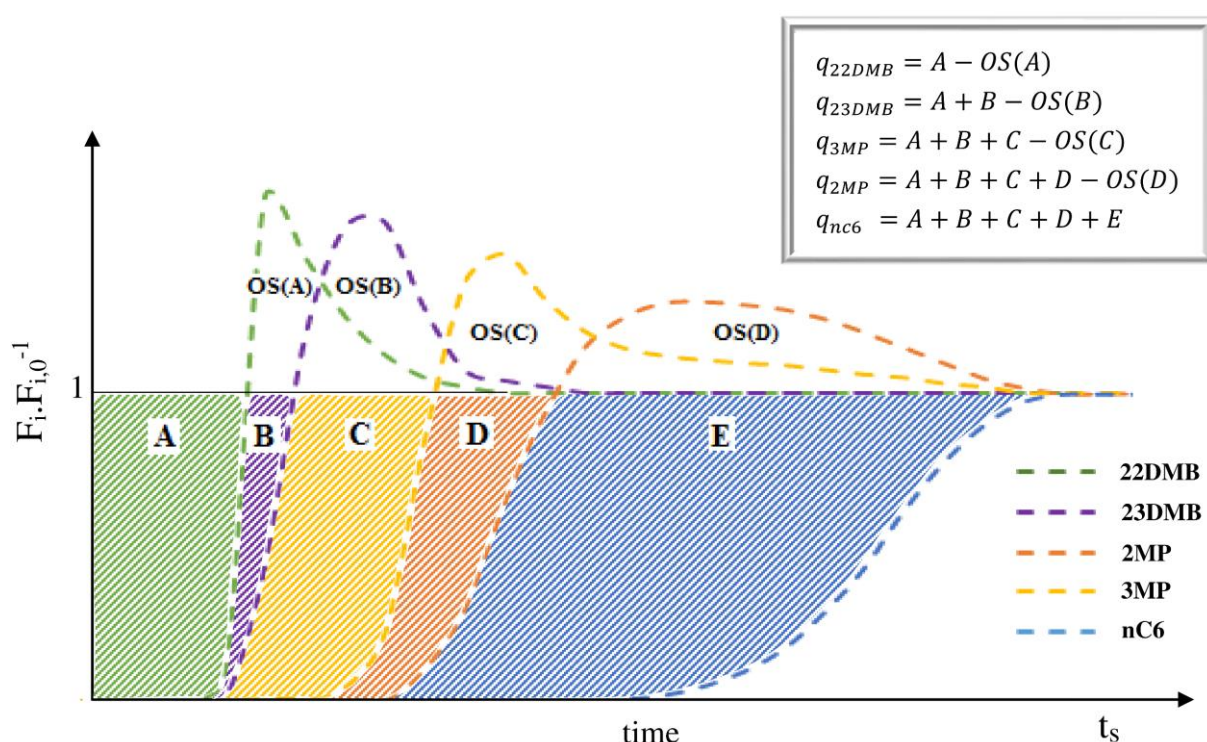


Figure 3.6 | Schematic representation showing a procedure to calculate the component loading of each isomer in a typical multicomponent breakthrough experiment (e.g., a mixture of hexane isomers).

3.2.2 Experimental Apparatus for Continuous Cyclic Studies

The experimental apparatus developed to perform continuous cyclic studies of a simplified two-step PSA with one single column is shown in Figure 3.7. As it can be seen, the unit is integrated into the screening apparatus system previously described by substituting/adding new devices and changing lines flux configurations. The core PSA unit consist on:

- 1) - A heating oven (*HO, FD 53, Binder*) assembled with an automatic 8-ports valve (*V3, VICI, Valco Instruments Co.*) was incorporated in the system, in which the AC is now operated. A stainless-steel column with a 0.42 m length and 0.01 m internal diameter was made to perform tests at a larger scale adsorbent amount level. The valve (*V3*) is used for switching between the adsorption and desorption steps in the cyclic operation;
- 2) - A diaphragm vacuum pump (*VP, N 810 FT.18, KNF*) was installed to depressurize the AC. Moreover, a manual flow metering valve (*V4, SS-SS1-VH, Swagelok*) was also used to control the level of vacuum pressure during the depressurization step;
- 3) - Two electronic pressure transducers (*PT1/PT2, PXM409-010BAUSBH, OMEGA*) were installed in the effluent lines of the AC, adsorption and desorption, to record the history of the pressure behaviour during the pressurization and depressurization stages;
- 4) - One temperature regulator (*TR, HT-MC1, Horst GmbH*) is used to heat trace the external lines between the HO and the preparative GC. These lines were insulated with ceramic wool and aluminium tape;
- 5) – The MFCs were upgraded for covering a higher flow rate range (*MFC1/MFC2, MC-100SCCM-D/5M, Alicat Scientific*);
- 6) - The flow paths in the valves (*V1/V2*) coupled to the preparative chromatography were adjusted. The valve (*V1*) was rearranged to switch between the AC bypass to check the paraffins vaporization stability on the TCD (preliminary step of the experiment) and send the alkane mixture to the HO. The valve (*V2*), adapted to act as a 4-ports valve, directs the AC output to the TCD and posterior analytical stage.



Figure 3.7 | Real view of the screening apparatus upgraded to perform adsorption studies on continuous cyclic operation: a) front view of the complete experimental unit; a1) close-up of the new devices incorporated on the system, showing MFC, PT, VP, valve (V3), TR and heat traced lines, and a2) internal view new HO assembled with a switching valve (V3) and CA.

Figure 3.8, panels a), b), and c), shows the schematic diagram of the homemade experimental apparatus, which consists of three main sections: (i) gas preparation, (ii) adsorption (pressurization and feed + analysis), and (iii) desorption (vacuum countercurrent depressurization followed by inert He purge + analysis), respectively. To better understand, each panel is illustrated with the valves in the correct position to perform a complete experiment. It is also important to highlight that the enumeration of the valves presented in the schematic diagram was corrected for the actual system. Therefore, the (V3) and (V4) nomenclature are attributed to the automatic 8-ports and manual flow metering valves, respectively.

The gas preparation section (panel a)) is similar to the one used for the screening studies, where the carrier gas (He) enters the system by different lines. After that, the SP continuously introduces the paraffins into the He stream, controlled by MFC1, to run through the packed injector in the preparative GC. Then, the vaporized mixture passes through the valve (V1), mixes with the He make-up line, and goes directly to the TCD. Simultaneously, the pure He, controlled by the MFC2, runs into the switching valve (V3), AC, VP, valve (V2) and leaves the system through the preparative GC vent line. When the vaporized mixture reaches the equilibrium state, the switching valve (V1) is actuated, and the mixture goes to the HO and leaves the system by the vent line.

As soon as the paraffin mixture fills the heat traced line between the preparative GC and HO, and the inert baseline in the TCD is reached (He make-up line), the adsorption section takes place, for which the experiment can be started. Therefore, two valves must be actuated simultaneously at time zero: (V3) and (V2). The feed mixture (panel b)) passes through the AC, and its effluent goes to the preparative GC, runs into the valve (V2), which is now in the position to send the mixture to the TCD, and flows through the TL line to the analytical GC for evaluation. The analytical procedure is the same as the one applied for the screening studies.

When the adsorption step finishes, the desorption stage occurs. For that, both valves (V2) and (V3) are again simultaneously actuated (panel c)). The AC is then countercurrent depressurized (to 10.1 kPa) with the VC and purged with the He stream from MFC2. The effluent passes through the valve (V2) and is sent to the analytical section for chromatographic evaluation. Once the desorption time is up, another cycle can be started. This overall procedure is performed until reaching the cyclic steady state.

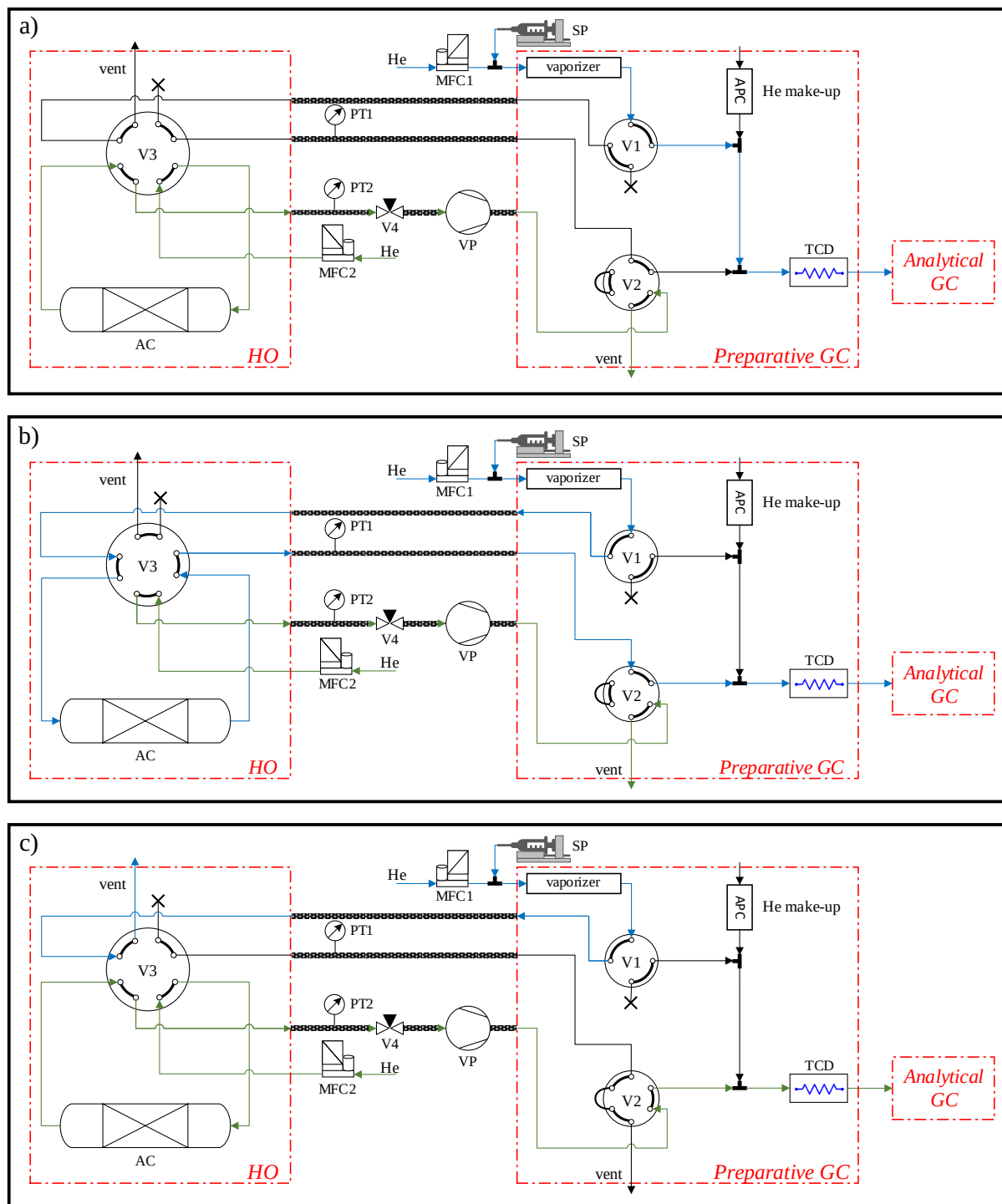


Figure 3.8 | Schematic diagram of the experimental apparatus developed to perform adsorption studies on continuous cyclic operation: a) gas preparation section for checking the vaporization of the paraffin mixture; b) pressurization and feed (adsorption); and c) vacuum countercurrent depressurization followed by inert He purge. Blue and green lines represent the paraffins (adsorption) and He purge (desorption) flow paths inside the system, respectively.

It is important to note that the AC is at atmospheric pressure in the first adsorption step, i.e., time zero of the experiment. The VC is turned on just a few moments before starting the first desorption step and then is kept on until finishing the experiment. Therefore, from the second until the last cycle, the AC, depressurized from the previous desorption step, is pressurized with the feed mixture followed by adsorption.

This system is also automated, being the switching valve (V3) incorporated in the software shown in Figure 3.3. Both valves (V2) and (V3) are programmed to simultaneously change their position at each predetermined time of adsorption and desorption step. Meanwhile, the sampling valve (which is now enumerated as V5) on the analytic GC continuously collects effluent samples to be analysed. The PTs connect directly to the PC via a USB control module, and the free OMEGA PC software records their digital data.

All the lines connected in the valve (V3) coupled in the HO are in 1/8" of external diameter (Figure 3.7 panel a2)), while the heat traced lines are in 1/16" diameter.

3.2.3 General Experimental Procedures and Working Conditions

The quality of the experimental results depends on the correct starting. Therefore, before executing an experimental run, some basic procedures were implemented ("start-up"). The first step before screening an adsorbent was to prepare the column, i.e., activating the material at high temperature to remove any pre-adsorbed moisture. The adopted procedures for the screening and cyclic studies were:

- i) For the screening studies, the solid was dried inside the AC in the preparative GC at a fixed temperature (depending on the material to be tested) for at least 12 h under pure He flow (5 ml.min⁻¹) and vacuum. The heating of the AC is performed with a ramp at 0.5 K.min⁻¹ programmed in the YL-Clarity software. For the cooling of the AC, a ramp of 2 K.min⁻¹ was applied;
- ii) For the cyclic studies, the solid was dried inside the AC in the HO at a fixed temperature for at least 12 h under pure He flow (10 ml.min⁻¹) in vacuum atmosphere. The heating and cooling of the AC were performed with a ramp at 1 and 2 K.min⁻¹, respectively.

On the AC preparation, glass wool was used at both ends to prevent any small particles from dragging and getting stuck in the lines.

The second step was to check the stabilization of the MFCs to operate accurately. For that, a manual bubble flowmeter (*BF, 10CC EA, Supelco*) was used to check each MFC's setpoint flow rate. Finally, the third and fundamental step, previously mentioned, is checking the paraffins vaporization through AC bypassing to ensure that the vaporization of the mixture is in an equilibrium state. For multicomponent experiments, after the concentration reaches a constant signal in the TCD, a few samples were chromatographically analysed in the CC and FID to guarantee that all components were completely vaporized, showing equal and constant peaks along with time.

In order to achieve a thermal equilibrium in the overall system, the temperatures of the packed inlet injector, TCD filament, TR to heat external lines, and capillary injector are equal and the same as those from the oven in which the AC operates. Only the FID detector runs with a different temperature, always 473 K, to produce its flame. The APC systems work at a constant flow rate mode. He flow rates of 40 ml.min⁻¹ are used on the make-up line and reference side of TCD. For the packed inlet injector, there is no need for a carrier make-up stream. For the analytic GC, 37 ml.min⁻¹ of H₂, 300 ml.min⁻¹ of air, and 22 ml.min⁻¹ of He make-up were set for the FID. Moreover, a split ratio of 200:1 and 300:1 was used in the capillary injector for the screening and cyclic studies, respectively. Finally, only 0.55 ml.min⁻¹ of the sample is sent to the CC for analysis.

The 6-ports sampling valve from the analytical section, responsible for sending an aliquot of the AC effluent gas to the CC, was optimized to capture and inject samples for alkane isomers mixtures at each minute and constant pressure. Therefore, the valve is temporized to cyclically actuate 20 s in the inject position and 40 s in the load position, where the loop is filled with the AC column effluent. Particularly, for septenary mixtures of pentane and hexane isomers, the cycles comprise 1.5 minutes, 30/60 s in load and inject position, respectively.

For the whole adsorption study, all paraffin isomers were of analytical grade with 99+% purity. *Sigma Aldrich* supplied all hexane isomers, while *Riedel-de Haën* and *Fluka* supplied nC5 and iC5, respectively. For the gases, *Linde* supplied He with 99.9996% purity and air (reconstituted air K with a concentration of 80% N₂ and 20% O₂), while *Alpha Gaz* supplied H₂ with 99.9999% purity.

3.3 Adsorption Metrics

For evaluating the different adsorbents studied in this work, three metrics were adopted: the average RON value of the mixture at the outlet of the bed, the ideal adsorption productivity at a fixed RON value and the adsorption selectivity.

3.3.1 RON

The real-time (instantaneous) RON of the alkane mixture leaving the adsorption column is calculated from the pure component RON_i (Table 1.1, *Chapter 1*) averaged over the exit gas composition, as follows:

$$Average\ RON = \frac{\sum_{i=1}^{N_c} (y_i \times RON_i)}{\sum_{i=1}^{N_c} y_i} \quad (3.3)$$

where y_i is the molar fraction of component i in the gas mixture at the outlet of the adsorption column and N_c is the number of components in the gas mixture.

3.3.2 Ideal Adsorption Productivity

A realistic comparison of relevance to industrial applications can be performed by comparing the ideal adsorbent productivity at an accumulated RON of 92. It represents the number of moles of the product obtained per cubic decimetre of adsorbent in a packed bed column completely clean at the beginning of an adsorption step.⁸ Therefore, to calculate the ideal productivity, the real-time RON of the alkane mixture leaving the adsorption column (Eq. 3.3) is averaged for the appropriate time interval until the desired 92 RON product is recovered. The volumetric productivity, P_s ($mol.dm^{-3}$), is then obtained by multiplying the gravimetric productivity (calculated through a material balance over the column) by the apparent particle density of the shaped material, ρ_a ($kg.dm^{-3}$), as follows:

$$P_s = \left\{ \sum_{i=1}^{N_c} \left[\frac{1}{m_s} \left(\int_0^{t_{RON92}} F_i dt - \varepsilon_b V_c C_{f,i} \right) \right] \right\} \cdot \rho_a \quad (3.4)$$

where t_{RON92} (s) is the time interval in which the 92 RON value is obtained.

3.3.3 Adsorption Selectivity

One of the objectives of this work is to separate pentane and hexane isomers into HRON and LRON fractions. Therefore, a convenient definition of adsorption selectivity, S , for experiments performed with equimolar mixtures, is the ratio of the loadings between LRON paraffins over the HRON ones according to the following equation:¹¹

$$S = \frac{q_{nC5} + q_{nC6} + q_{2MP} + q_{3MP}}{q_{iC5} + q_{23DMB} + q_{22DMB}} \quad (3.5)$$

This definition is applied for adsorbent materials exhibiting a separation based on thermodynamic equilibrium associated with a normal adsorption hierarchy (following the normal boiling point order of the compounds closely), wherein the adsorption strength of isomers species decreases as the degree of branching increases.

3.4 Modelling Adsorption Equilibrium Isotherms

Aside from establishing a proper correlation for the equilibrium data for a given adsorbent material, the compliance of these data to a suitable isotherm model is very important. Several theories of adsorption equilibrium based on different fundamental approaches have been formulated giving rise to different types of isotherms, some of which are based on fundamental laws of thermodynamics, and some are purely empirical.¹²⁻¹⁴ The different equation parameters and the underlying thermodynamic assumptions of these models can provide critical information into the sorption mechanism pathways, adsorbent surface properties, maximum adsorption capacity of the adsorbent for a particular adsorbate species, adsorbent-adsorbate affinity, and also the heats of adsorption.

In this work, we mainly focus on the analysis of type I isotherms since they are completely related to the adsorption of pentane and hexane isomers on microporous adsorbents. The following subsections briefly describe some models considered relevant for correlating the thermodynamic data collected through the present study. Certainly, other more refined models can be considered. However, it is worth mentioning that the complex multicomponent sorption of five or even seven alkane isomers in MOFs or carbon materials can be a cumbersome task and should be made within the scope of a new, utterly re-oriented research, which is outside the proposed objectives.

3.4.1 Langmuir isotherm

The Langmuir isotherm is the simplest theoretical model for monolayer adsorption.¹⁵ The model was deduced based on the following assumptions: (i) the adsorbent surface is energetically homogeneous (adsorption energy is constant over all sites), (ii) adsorption on the surface is localized (adsorbed molecules are immobile), (iii) each site can accommodate only one molecule, and (iv) there are no interactions between adsorbed molecules on neighbouring sites.²

The Langmuir isotherm is described as follows:

$$q = q_{sat} \frac{(bp)}{1 + (bp)} \quad (3.6)$$

where q ($mol.kg^{-1}$) is the loading on the adsorbent surface at equilibrium conditions, q_{sat} ($mol.kg^{-1}$) is the saturation loading capacity (maximum adsorbed concentration corresponding to a complete monolayer coverage), b (kPa^{-1}) is the affinity constant, which measures how strong an adsorbate molecule is attracted onto a surface, and p (kPa) is the partial pressure of adsorbate species.

The temperature dependence of the affinity constant follows a Van't Hoff equation:²

$$b = b_{\infty} \exp\left(\frac{-\Delta H}{RT_s}\right) \quad (3.7)$$

where b_{∞} (kPa^{-1}) is the affinity constant at infinite temperature, ΔH ($J.mol^{-1}$) is the heat of adsorption, R ($J.mol^{-1}.K^{-1}$) is the universal gas constant, and T_s (K) is the temperature of the adsorbent.

Although the original model assumes that q_{sat} is constant and does not change with temperature (representing a fixed number of surface sites), the idea of its temperature dependence has been supported by some authors. According to Malek and Farooq,¹⁶ this is usually considered to account for the thermal expansion of adsorbate species, which decreases the monolayer coverage with increasing the temperature. Do¹⁷ proposed the following equation:

$$q_{sat} = q_{sat,0} \exp\left[\delta \left(1 - \frac{T_s}{T_{s,0}}\right)\right] \quad (3.8)$$

where $q_{sat,0}$ ($mol.kg^{-1}$) is the saturation loading capacity at some adsorbent reference temperature $T_{s,0}$ (K) and δ is the thermal expansion factor of adsorbate species.

At high sorbate concentration, the Langmuir isotherm approaches to a constant monolayer since at saturation $p \rightarrow \infty$, $q \rightarrow q_{sat}$, and $\theta \rightarrow 1$. Alternatively, at low sorbate concentration, it reduces to a linear form and thus follows Henry's law:²

$$q = (q_{sat}b)p = Hp \quad (3.9)$$

where H ($mol.kg^{-1}.kPa^{-1}$) is the Henry's constant.

The Langmuir equation can readily be extended to multicomponent systems based on the parameters obtained for each component of the mixture. Accordingly, the loading of component i , q_i , in a mixture is given by:

$$q_i = q_{sat,i} \frac{(b_i p_i)}{1 + \sum_{j=1}^{N_c} (b_j p_j)} \quad (3.10)$$

3.4.2 DSL Isotherm

The Langmuir theory can also be applied to describe the adsorption phenomena on surfaces that offer more than one type of elementary binding sites. Considering two-types of binding sites, the contribution of each site to the total loading is simply additive, leading to the DSL isotherm.¹⁷ All of the assumptions of the Langmuir model apply to each site. Furthermore, the sites are independents (do not interact with each other) and energetically different. The adsorption isotherm is defined as:

$$q = \left(q_{sat,1} \frac{(b_1 p)}{1 + (b_1 p)} \right)_{site\ 1} + \left(q_{sat,2} \frac{(b_2 p)}{1 + (b_2 p)} \right)_{site\ 2} \quad (3.11)$$

The overall Henry's constant is the sum of those on each particular adsorption site:

$$H = (q_{sat,1} b_1)_{site\ 1} + (q_{sat,2} b_2)_{site\ 2} \quad (3.12)$$

For predicting multicomponent isotherms, the DSL model can be extended to:

$$q_i = \left(q_{sat,1,i} \frac{(b_{1,i} p_i)}{1 + \sum_{j=1}^{N_c} (b_{1,j} p_j)} \right)_{site\ 1} + \left(q_{sat,2,i} \frac{(b_{2,i} p_i)}{1 + \sum_{j=1}^{N_c} (b_{2,j} p_j)} \right)_{site\ 2} \quad (3.13)$$

3.4.3 Sips (Langmuir-Freundlich) Isotherm or Loading Ratio Correlation (LRC)

The Sips isotherm is a hybrid model that combines the Langmuir and Freundlich isotherms, being deduced to predict adsorption in heterogeneous systems.¹⁸ It is represented by the following general equation:¹⁷

$$q = q_{sat} \frac{(bp)^{\frac{1}{n}}}{1 + (bp)^{\frac{1}{n}}} \quad (3.14)$$

where the parameter n characterizes the system heterogeneity, which could stem from the solid (structural/energetical property) or the adsorbate or a combination of both. The larger this parameter, the more heterogeneous the system is. When n is equal to 1, the model reduces to Langmuir isotherm.

The temperature dependence forms of b and q_{sat} are those from the Langmuir isotherm, while for the exponent n may take the following empirical form:

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_{s,0}}{T_s} \right) \quad (3.15)$$

where n_0 is the parameter n at some reference temperature and α is a constant parameter.

For multicomponent systems, the extended Sips isotherm can be applied in analogy to the extended Langmuir form:¹⁹

$$q_i = q_{sat,i} \frac{(b_i p_i)^{\frac{1}{n_i}}}{1 + \sum_{j=1}^{N_c} (b_j p_j)^{\frac{1}{n_j}}} \quad (3.16)$$

3.4.4 Error Estimation

The corresponding parameters from the isotherm models were determined through an optimization procedure that minimizes the mean relative deviation, $\bar{\Delta}q$, between the experimental data and model predictions as a convergence criterion. The error estimation is represented by the following equation:¹³

$$\bar{\Delta}q = \frac{1}{N} \sqrt{\sum_{i=1}^N \left(\frac{(q_{exp} - q_{model})}{q_{exp}} \right)^2} \quad (3.17)$$

where N is the total number of data points (experimental loadings).

3.5 Mathematical Modelling of Fixed Bed Adsorption Dynamics

The design of an adsorptive separation process requires the development of a mathematical model capable of describing conveniently the dynamic behaviour of the fixed bed adsorption system.²⁰ An adequate model provides: (i) flexibility to run multiple simulations that can help the analysis of the experimental data with a different combination of thermodynamic isotherm models, axial dispersion and mass transfer correlations, (ii) analyse temperature profiles and their influence on the overall dynamics, and (iii) predict answers for any defined changes in the process variables and parameters (e.g., temperature, pressure, total gas flow rate, feed concentration, and bed dimensions).^{21,22} Thus, a predictive model using independently established equilibrium and kinetic data is essential, playing a key role in the technology transfer from laboratory to industrial scale. It may offer, in principle, a method for reducing the extensive experimentation needed to evaluate the overall column dynamics under diverse conditions, which generally tends to be laborious, expensive, and time-consuming.²³

Motivated by this, a general mathematical model has been developed to simulate and analyse the transient adsorption behaviour of pentane and hexane isomers observed on the experimental breakthrough measurements. Fixed bed adsorption models have their origins in the fundamental partial differential equations (PDEs) distributed over time and space according to the material, energy, and momentum conservation laws. Moreover, they are augmented by transport rate and equilibrium isotherm equations.²⁰ However, due to the complexities associated with the simultaneous solution of the coupled system of PDEs, simplified models that provide a good compromise between accuracy and computational effort are desirable. In this way, it is crucial to recognize the characteristics of the system under study, to develop a comprehensive model that is neither unnecessarily complex nor oversimplified, but with the basics to capture the overall dynamics.

Let us consider a fixed bed adsorption system in which an inert carrier gas flows at steady state. At time zero, a mixture of paraffins isomers with known composition, diluted in

the inert carrier gas, is introduced at the inlet of the column and fed until the saturation of the bed. After the breakthrough is complete, the paraffins mixture is withdrawn from the feed, and the regeneration of the bed is performed by purging the column with the inert carrier gas. The following additional assumptions were introduced:

- 1) The gas phase follows the ideal gas law;
- 2) The system operates under constant total pressure, meaning that the frictional pressure drop across the bed can be assumed as negligible. This is a reasonable assumption for small scale laboratory units that work with a few mg or g of adsorbent samples;
- 3) The flow pattern of the gas phase across the bed is described by the axial dispersed plug flow model;
- 4) The mass transfer from the gas to the solid phase is represented by a linear driving force (LDF) constant rate approximation, which is based on a solid phase concentration gradient;²⁴
- 5) The adsorption equilibrium can be described by one of the isotherms models mentioned in the above Section 3.4;
- 6) The system can be adiabatic or isothermal, or non-isothermal/non-adiabatic. For non-isothermal working conditions, a heterogeneous energy balance inside the column is considered, with the temperature of the gas and solid phase being taken into account separately. An independent equation is formulated for each phase, which is coupled to each other through a film heat energy transfer. The temperature variation of the column wall is neglected, which is also a reasonable approximation for small laboratory adsorption columns inside a sophisticated temperature-controlled chromatographic oven (operating with forced convection);
- 7) Radial velocity, concentration, and temperature gradients across the bed are negligible. Generally, detailed balance equations including radial dispersion are not necessary in small diameter adsorption columns;²
- 8) The adsorbent particles are considered spherical and homogeneous in size and density. Moreover, they are packed uniformly into the bed (bed void fraction constant);
- 9) There are no temperature gradients in the solid phase, e.g., the temperature within the particle is uniform;
- 10) The physical properties of the gas phase across the bed are those of the feed gas, and the physical properties of the solid phase are constant;

11) The bed is tubular with a constant cross-section area.

Based on the above assumptions, the one-dimensional fixed bed column model can be formulated in a reasonable way by the following equations:

Ideal Gas Law

The bulk gas phase follows the ideal gas law, which expresses the relation between the total concentration of all components (inert + sorbate species) in the gas mixture, C_T (mol.m^{-3}), the total pressure, P_T (kPa), and the temperature in bulk gas phase, T_g (K), according to the following equation of state:

$$C_T = \frac{P_T}{RT_g} \quad (3.18)$$

In addition, the density of the gas mixture composition, ρ_g (kg.m^{-3}), can be obtained by multiplying C_t with the average molar mass of the gas mixture, M_m (kg.mol^{-1}):²⁵

$$\rho_g = C_T M_m = \frac{P_T}{RT_g} \sum_{i=1}^{N_c} y_i M_i \quad (3.19)$$

where M_i (kg.mol^{-1}) is the molar mass of component i .

Mass Balance to Adsorbable Species

The transient gas phase component mass balance, which includes the effect of the axial dispersion, convection flow term, gas phase mass accumulation, and a mass transfer rate term from the bulk fluid phase to the solid phase, is expressed by the following equation for a differential axial position in the bed, ∂z , at an instant time, ∂t , (control volume) of the adsorption column:

$$\varepsilon_b D_{ax} \frac{\partial}{\partial z} \left(C_T \frac{\partial y_i}{\partial z} \right) = \frac{\partial}{\partial z} (F_T y_i) + \varepsilon_b \frac{\partial}{\partial t} (C_T y_i) + \rho_b \frac{\partial \bar{q}_i}{\partial t} \quad (3.20)$$

where F_T ($\text{mol.m}^{-2}.\text{s}^{-1}$) is the total molar flux of the gas mixture, ρ_b (kg.m^{-3}) is the bulk density, $\bar{q}_i$ (mol.kg^{-1}) is the averaged loading of component i within the adsorbent,

D_{ax} ($m^2 \cdot s^{-1}$) is the axial mass dispersion coefficient, z (m) is the distance along the length of the column (axial coordinate), and t (s) is the time.

The Danckwerts boundary conditions for a dispersed plug flow system are used at the column's inlet (Eq. 3.20a) and the outlet (Eq. 3.20b).²⁶ Due to the axial diffusion, the molar fraction of the component i within the entrance of the bed is different from the one in the entering stream. At the outlet, the concentration gradient is assumed to be zero, and therefore the molar fraction of the component i is finite:

$$z = 0; t > 0 \quad \varepsilon_b D_{ax} C_T \frac{\partial y_i}{\partial z} = F_T (y_i - y_{i,f}) \quad (3.20a)$$

$$z = L; t > 0 \quad \frac{\partial y_i}{\partial z} = 0 \quad (3.20b)$$

where, $y_{i,f}$ is the molar fraction of component i in the feed composition (inlet of the column), and L (m) is the length of the column.

Overall Mass Balance

The overall material balance in the adsorption column accounts for the total mole flux variations in the fixed bed. Accordingly, the governing partial differential equation is written as follows:

$$\frac{\partial F_T}{\partial z} + \varepsilon_b \frac{\partial C_T}{\partial t} + \rho_b \sum_{i=1}^{N_c} \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (3.21)$$

The boundary condition for a clean column subjected to a step change of adsorbable components at the inlet is:

$$z = 0; t > 0 \quad F_T = F_{T,f} \quad (3.21a)$$

where, $F_{T,f}$ ($mol \cdot m^{-2} \cdot s^{-1}$) is the total molar flux of the gas mixture in the feed.

Mass Transfer Rate

The transport of the adsorbable species from the bulk gas phase to the solid phase is expressed by the LDF rate approximation shown in Eq. 3.22.²⁴ Hence, the adsorption rate of component i into adsorbent particles is essentially proportional to the linear difference between its concentration at the outer surface of the particle (solid-fluid interface in equilibrium conditions) and within the particle (volume-averaged loading):

$$\frac{\partial \bar{q}_i}{\partial t} = k_{LDF,i}(q_i - \bar{q}_i) \quad (3.22)$$

where $k_{LDF,i}$ (s^{-1}) is the lumped mass transfer coefficient of component i .

The temperature dependence of the $k_{LDF,i}$ coefficient follows the Arrhenius form:¹⁷

$$k_{LDF,i} = k_{LDF\infty,i} \exp\left(\frac{\Delta E_i}{RT_s}\right) \quad (3.23)$$

where $k_{LDF\infty,i}$ (s^{-1}) is the LDF mass transfer coefficient at infinite temperature and ΔE_i ($J.mol^{-1}$) is the activation energy of component i .

This simple linear rate approach for adsorption/desorption is used due to the difficulties of correctly discriminating the true mass transfer mechanisms in such a complex system accounting for the transport of several compounds (pentanes/hexanes) in the adsorbent pore network. Otherwise, independent kinetic experiments should be done. Therefore, the values calculated in such a way are empirical, but they provide a reliable time constant for the mass transfer of each system studied. Also, they can be compared to other effects, such as the axial dispersion or residence time of the gas in the bed, that determine the efficiency of the breakthrough curves.

Energy Balance: Gas Phase

The gas phase energy balance, which includes axial thermal conduction, convection of energy, thermal accumulation in the gas phase, heat transfer between gas and solid through a laminar film, and the energy transferred to the column wall, is described by:

$$\begin{aligned}
& K_{ax} \frac{\partial^2 T_g}{\partial z^2} \\
& = F_T c_{pg} \frac{\partial T_g}{\partial z} + \varepsilon_b C_T c_{pg} \frac{\partial T_g}{\partial t} + (1 - \varepsilon_b) a_s h_f (T_g - T_s) + a_{ac} h_w (T_g - T_w)
\end{aligned} \tag{3.24}$$

where K_{ax} ($W \cdot m^{-1} \cdot K^{-1}$) is the axial heat dispersion coefficient, c_{pg} ($J \cdot mol^{-1} \cdot K^{-1}$) is the heat capacity of the gas mixture, h_f ($W \cdot m^{-2} \cdot K^{-1}$) is the film heat transfer coefficient between the gas and adsorbent, h_w ($W \cdot m^{-2} \cdot K^{-1}$) is the internal convective heat transfer coefficient between the gas and column wall, T_w (K) is the temperature of the column wall, a_s (m^{-1}) is the specific area of the adsorbent (expresses the ratio of the particle external surface area to volume, in which for spherical particles: $a_s = 3/R_s$), and a_{ac} (m^{-1}) is the specific area of the adsorption column ($a_{ac} = 2/R_{ac}$). Here, R_p and R_{ac} denote for the radius (m) of the adsorbent particle and column, respectively.

Since the convective transport of mass and heat occur by similar mechanisms, the following boundary conditions are applied by analogy with the Danckwerts boundary conditions.

$$z = 0; t > 0 \quad K_{ax} \frac{\partial T_g}{\partial z} = F_T c_{pg} (T_g - T_{g,f}) \tag{3.24a}$$

$$z = L; t > 0 \quad \frac{\partial T_g}{\partial z} = 0 \tag{3.24b}$$

where $T_{g,f}$ (K) is the temperature of the gas mixture is the feed.

Energy balance: Solid Phase

The solid phase energy balance, including thermal accumulation in the solid phase, the gas-solid film heat transfer, and the heat generated by the adsorption of component i , is represented by:

$$\rho_a c_{ps} \frac{\partial T_s}{\partial t} = a_s h_f (T_g - T_s) + \rho_a \sum_{i=1}^{N_c} (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \tag{3.25}$$

where c_{ps} ($J \cdot kg^{-1} \cdot K^{-1}$) is the heat capacity of the adsorbent.

Initial conditions

Initially, the column is filled with the inert gas and does not contain any other component; the bed is completely regenerated, which means that the loading concentration of each sorbate species in the solid is zero; the total pressure is constant; and there is thermal equilibrium between the gas phase, solid phase and the wall of the column, all being equal to the feed gas temperature. Mathematically, such conditions are expressed with the equations below:

$$\begin{aligned}
 t = 0 ; \forall z ; y_{inert} &= 1 \\
 t = 0 ; \forall z ; y_i = \bar{q}_i &= 0 \quad \text{for } i \neq inert ; \\
 t = 0 ; \forall z ; F_T = F_{T,f} ; C_T &= C_{T,f} \\
 t = 0 ; \forall z ; T_g = T_s = T_w &= T_{g,f}
 \end{aligned} \tag{3.26}$$

3.5.1 Transport Parameters

3.5.1.1 Axial Mass Dispersion

The axial mass dispersion coefficient, D_{ax} , is calculated accounting for the molecular diffusion and turbulent mixing arising the splitting and recombination of flows around the adsorbent particles:²

$$D_{ax} = \gamma_1 D_m + \gamma_2 d_s v_{int} \tag{3.27}$$

where D_m ($m^2.s^{-1}$) is the molecular diffusion coefficient, d_s (m) is the diameter of the adsorbent particle, and v_{int} ($m.s^{-1}$) is the interstitial velocity of the gas mixture. The constants γ_1 and γ_2 account for the bed tortuosity and turbulent mixing, respectively, and typical values of 0.7 and 0.5 are used.

3.5.1.2 Molecular Diffusion

The molecular diffusivity for the component i is approximated using the correlation verified by Fairbanks and Wilke:²⁷

$$D_{m,i} = \frac{(1 - y_i)}{\sum_{\substack{j=1 \\ j \neq i}}^{N_c} \frac{y_j}{D_{ij}}} \quad (3.28)$$

where $D_{ij} (m^2 \cdot s^{-1})$ is the binary diffusivity of component i with respect to each component of the mixture, which is estimated from the Chapman-Enskog equation:²⁸

$$D_{ij} = 1.8583 \times 10^{-7} \sqrt{T_g^3 \left(\frac{1}{M_i} + \frac{1}{M_j} \right) \frac{1}{P_t \sigma_{ij}^2 \Omega_{D_{ij}}}} \quad (3.29)$$

here, the units should be: T_g (K), M_i and M_j ($g \cdot mol^{-1}$) and P_t (atm). For the calculations, it was assumed that $1 \text{ atm} \approx 100 \text{ kPa}$.

The Lennard-Jones parameter σ_{ij} (collision diameter, Å) is defined by:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (3.30)$$

The collision integral for diffusion $\Omega_{D_{ij}}$ is a dimensionless function of the temperature and the Lennard-Jones parameter ε_{ij}/κ (maximum energy of attraction between molecular pairs, K). It is computed using the Neufeld et al.²⁹ correlation:

$$\Omega_{D_{ij}} = \frac{A}{T^{*B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \quad (3.31)$$

$$\begin{aligned} A &= 1.06036, & C &= 0.19300, & E &= 1.03587, & G &= 1.76474 \\ B &= 0.15610, & D &= 0.47635, & F &= 1.52996, & H &= 3.89411 \end{aligned}$$

with:

$$T^* = \frac{\kappa T_g}{\varepsilon_{ij}}, \quad \frac{\varepsilon_{ij}}{\kappa} = \frac{\sqrt{\varepsilon_i \varepsilon_j}}{\kappa} \quad (3.32)$$

where T^* is the dimensionless temperature, and κ ($J \cdot K^{-1}$) is the Boltzmann's constant.

The Lennard-Jones parameters σ_i and ε_i/κ , for each gas molecule, are summarised in Table 3.1.

Table 3.1 | Lennard Jones parameters.

Substance	Lennard-Jones parameters		Ref.
	σ (Å)	ε/κ (K)	
He	2.5510	10.220	29
nC5	5.85	326	28
iC5	5.8120	327	28
nC6	5.9490	339.30	29
2MP	8.0650	267	30
3MP	8.5870	265	30
23DMB	6.7510	412	30
22DMB	7.6140	266	30

3.5.1.3 Viscosity

The viscosity of the gas mixture, μ_g (Pa.s), is estimated from the following semi-empirical equation:²⁸

$$\mu_g = \sum_{i=1}^{N_c} \frac{y_i \mu_i}{\sum_{j=1}^{N_c} y_j \phi_{ij}} \quad (3.33)$$

where μ_i (Pa.s) is the viscosity of component i , defined in terms of the Lennard-Jones parameters by:²⁸

$$\mu_i = 2.6693 \times 10^{-6} \left(\frac{\sqrt{M_i T_g}}{\sigma_{ij}^2 \Omega_\mu} \right) \quad (3.34)$$

here, the units should be: T_g (K) and M_i (g.mol⁻¹).

The collision integral for viscosity Ω_μ varies with the dimensionless temperature following the empirical correlation proposed by Neufeld et al.:²⁹

$$\Omega_\mu = \frac{A}{T^{*B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)}$$

$$A = 1.16145, \quad C = 0.52487, \quad E = 2.16178 \quad (3.35)$$

$$B = 0.14874, \quad D = 0.77320, \quad F = 2.43787$$

The dimensionless quantities, Φ_{ij} , shown in Eq. 2.39 are given by:²⁸

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-\frac{1}{2}} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2 \quad (3.36)$$

3.5.1.4 Heat Capacity

The heat capacity of the gas mixture, c_{pg} ($J \cdot mol^{-1} \cdot K^{-1}$), is expressed via a weighted average on a molar basis:³¹

$$c_{pg} = \sum_{i=1}^{N_c} y_i c_{pi} \quad (3.37)$$

where c_{pi} ($J \cdot mol^{-1} K^{-1}$) is the heat capacity at a constant pressure of component i , determined by the polynomial equation:³²

$$c_{pi} = \sum_{i=0}^3 CP_i T_g^i = CP_0 + CP_1 T_g + CP_2 T_g^2 + CP_3 T_g^3 \quad (3.38)$$

where CP_i are the empirical constants of component i , which are reported in Table 3.2.

Table 3.2 | Heat capacities constants.³²

Substance	CP_0 ($J \cdot mol^{-1} \cdot K^{-1}$)	CP_1 ($J \cdot mol^{-1} \cdot K^{-2}$)	CP_2 ($J \cdot mol^{-1} \cdot K^{-3}$)	CP_3 ($J \cdot mol^{-1} \cdot K^{-4}$)
He	2.080×10^1	-	-	-
nC5	-3.626×10^0	4.873×10^{-1}	-2.580×10^{-4}	5.305×10^{-8}
iC5	-9.525×10^0	5.066×10^{-1}	-2.729×10^{-4}	5.723×10^{-8}
nC6	-4.413×10^0	5.820×10^{-1}	-3.119×10^{-4}	6.494×10^{-8}
2MP	-1.570×10^1	6.184×10^{-1}	-3.573×10^{-4}	8.085×10^{-8}
3MP	-2.386×10^0	5.690×10^{-1}	-2.870×10^{-4}	5.033×10^{-8}
23DMB	-1.461×10^1	6.150×10^{-1}	-3.376×10^{-4}	6.820×10^{-8}
22DMB	-1.663×10^1	6.293×10^{-1}	-3.481×10^{-4}	6.850×10^{-8}

The specific heat capacity of the gas mixture, $\hat{c}_{pg}$ ($J \cdot kg^{-1} \cdot K^{-1}$), can be obtained from the ratio of the molar heat capacity to the molar mass of the mixture:²⁵

$$\hat{c}_{pg} = \frac{c_{pg}}{\sum_{i=1}^{N_c} y_i M_i} \quad (3.39)$$

3.5.1.5 Thermal Conductivity

The thermal conductivity of the gas mixture, k_g ($W \cdot m^{-1} \cdot K^{-1}$), is approximated by a method analogue to that previously given for viscosity (Eq. 3.33):²⁸

$$k_g = \sum_{i=1}^{N_c} \frac{y_i k_{g,i}}{\sum_{j=1}^{N_c} y_j \Phi_{ij}} \quad (3.40)$$

where $k_{g,i}$ ($W \cdot m^{-1} \cdot K^{-1}$) is the thermal conductivity of component i , expressed by the Eucken formula:²⁸

$$k_{g,i} = \left(\hat{c}_{pi} + \frac{5}{4} \frac{R}{M_i} \right) \mu_i \quad (3.41)$$

3.5.1.6 Axial Heat Dispersion

The axial heat dispersion coefficient, K_{ax} , is estimated using the correlation proposed by Votruba et al.,³³ applicable over a large range of Reynolds ($0.1 \leq Re \leq 1000$) numbers:

$$\frac{1}{Pe_h} = \frac{k_e^0/k_g}{RePr} + \frac{14.5}{d_p \left(1 + \frac{A}{RePr} \right)} \quad (3.42)$$

where k_e^0 ($W \cdot m^{-1} \cdot K^{-1}$) is the axial thermal conductivity in the stagnant bed, and A is a constant ranging from 0 to 5. According to the authors, 2.9 is a reasonable value of A for spherical particles. Here, d_p should be expressed in (mm).

The ratio k_e^0/k_g is calculated applying Krupickza's³³ correlation:

$$\frac{k_e^0}{k_g} = \left(\frac{k_s}{k_g} \right)^{0.28 - (0.757 \log \varepsilon_b) - (0.057 \log \frac{k_s}{k_g})} \quad (3.43)$$

where k_s ($W.m^{-1}.K^{-1}$) is the thermal conductivity of the adsorbent.

The dimensional axial heat Peclet, (Pe_h), Reynolds, (Re), and Prandtl, (Pr), numbers are defined as:

$$Pe_h = \frac{C_T c_{pg} v_{int} d_s}{K_{ax}} \quad (3.44)$$

$$Re = \frac{\rho_g v_{sup} d_s}{\mu_g} \quad (3.45)$$

$$Pr = \frac{\hat{c}_{pg} \mu_g}{k_g} \quad (3.46)$$

where v_{sup} ($m.s^{-1}$) is the superficial velocity of the gas mixture.

3.5.1.7 Film Heat Transfer Coefficient

The film heat transfer coefficient h_f ($W.m^{-2}.K^{-1}$) is estimated from the Nusselt number, (Nu), using the Wakao et al.³⁴ correlation:

$$Nu = \frac{h_f d_s}{k_g} = 2 + 1.1 Re^{0.6} Pr^{\frac{1}{3}} \quad (3.47)$$

Only two parameters must be estimated: (i) the mass transfer coefficient for each adsorbable component in the gas mixture and (ii) the internal convective heat transfer coefficient between the gas and column wall. Both coefficients were used as fitting parameters, i.e., they were obtained by matching the experimental breakthrough curves.

3.5.2 Numerical Solution of Model Equation

The numerical solution of the coupled system of fundamental parabolic partial differential equations (PDEs) was obtained applying the well-established method of lines (MOL).³⁵ The numerical procedure reduces the set of PDEs in space and time domains to a set of approximating ordinary differential/algebraic equations (ODEs) in time through the discretization of the spatial (boundary-value) derivatives (semi-discrete method). Then, the

resulting system of initial-value ODEs is solved numerically by an appropriate ODE integration routine.

In this work, the simulations were run on MATLAB R2016a software (The MathWorks, Inc.), a high-level matrix/array language with an interactive environment for technical computing.³⁶ Moreover, the package offers a set of adaptive step functions for solving ODEs and an extensive functionality that can be used to implement the MOL.³⁷

First, the spatial derivatives are approximated algebraically by finite differences (FDs) over a uniform grid, where the AC was divided into N equal increments ($\Delta z = L/N$), as shown in Figure 3.9. For each node, the material and energy balances equations are solved. The greater N , the more precise the numerical simulation. Five dss routines (differentiation in space subroutines), dss002 to dss010, are programmed to use second-order to tenth-order FD approximations. These routines can be found available for free on Schiesser's webpage.³⁸ Thereafter, the system of ODEs is solved by the stiff integrator ode15s, a variable order solver based on the numerical differentiation formulas (NDFs), which optionally uses the backward differentiation formulas (BDFs), also known as Gear's method.³⁷ The resolution occurs in multi-step with relative and absolute tolerances of 10^{-5} . The user defines the number of points and the dss routine order, where it was found that a mesh between 150 - 250 points in conjunction with a dss routine greater or equal to dss006 appeared to give satisfactory accuracy for most of the runs.

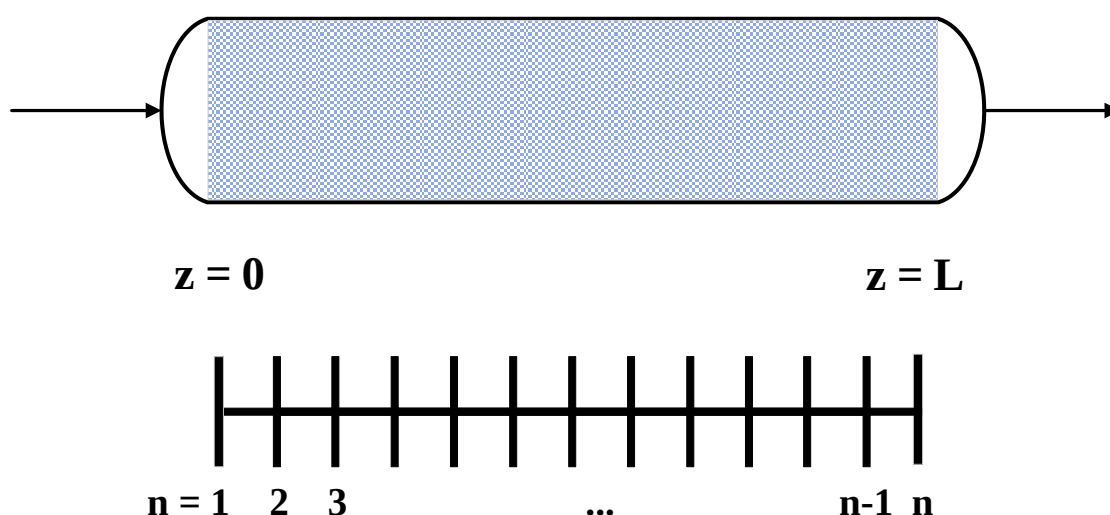


Figure 3.9 | Schematic representation of the 1D spatial discretization along with the AC.

The MOL has proven to be a powerful tool for solving PDEs, being widely used for simulating fixed bed adsorption. For instance, this method has already been applied for numerically studying the separations: carbon dioxide from nitrogen³⁹⁻⁴¹ and/or methane,^{41,42} oxygen from air,^{43,44} ethanol from water,⁴⁵ propane from propylene,⁴⁶ and pentane/hexane light naphtha fractions.^{46,47}

3.6 Conclusions

The fundamental tools that will be used in the following chapters for screening a series of adsorbent materials in order to improve the current TIP processes were presented. A new experimental apparatus was built for screening different microporous adsorbent materials for their ability to separate pentane and hexane isomers in a fixed bed adsorber. The adsorption unit allows measuring single and complex multicomponent transient breakthrough curves at industrially relevant separation conditions. The influence of temperature, alkane pressure, and total flow rates can be analysed to evaluate the dynamic behaviour of the packed bed adsorber systematically. Subsequently, the system was improved for working under continuous cyclic operation such as a simplified 2-steps PSA experiment: I - pressurisation and feed (adsorption), and II – vacuum countercurrent depressurisation followed by an inert purge (desorption).

At the same time, to analyse and interpret the experimental data obtained, a mathematical model was developed. Fundamental mass and energy balances, equilibrium isotherms, a linear rate expression to account for the mass transfer between the gas phase and the porous adsorbent, transport parameters, and initial and boundary conditions necessary to establish a fixed bed system are described in detail. The transport parameters of the model were determined based on the correlations available in the literature. The numerical package was developed in MATLAB code, with the solution of the coupled system of PDE equations performed through the MOL technique. The mathematical model will be a valuable tool to validate the experiments providing a clear understanding of the sorption mechanisms that govern the capability of the adsorbents to separate pentane and hexane isomers into HRON and LRON fractions.

3.7 References

- (1) Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworth, 1987.

- (2) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons, 1984.
- (3) Ruthven, D. M.; Farooq, S.; Knaebel, K. S. *Pressure Swing Adsorption*; VCH Publishers, 1994.
- (4) Ruthven, D. M. Adsorption, Fundamentals. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, 2001; Vol. 1, pp 582–617.
- (5) Silva, J. A. C.; Ferreira, A.; Mendes, P. A. P.; Cunha, A. F.; Gleichmann, K.; Rodrigues, A. E. Adsorption Equilibrium and Dynamics of Fixed Bed Adsorption of CH₄/N₂ in Binderless Beads of 5A Zeolite. *Ind. Eng. Chem. Res.* **2015**, *54*, 6390–6399.
- (6) Krishna, R. Methodologies for Evaluation of Metal-Organic Frameworks in Separation Applications. *RSC Adv.* **2015**, *5*, 52269–52295.
- (7) Gitis, V.; Rothenberg, G. *Handbook of Porous Materials: Synthesis, Properties, Modeling and Key Applications*; World Scientific Publishing Co Pte Ltd, 2021.
- (8) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels. *Science* **2013**, *340*, 960–964.
- (9) Worch, E. *Adsorption Technology in Water Treatment: Fundamental, Processes, and Modeling*; De Gruyter, 2012.
- (10) Helfferich, F.; Klein, G. *Multicomponent Chromatography - Theory of Interference*; Marcel Dekker, 1970; Vol. 4.
- (11) Dubbeldam, D.; Krishna, R.; Calero, S.; Yazaydin, A. Ö. Computer-Assisted Screening of Ordered Crystalline Nanoporous Adsorbents for Separation of Alkane Isomers. *Angew. Chemie - Int. Ed.* **2012**, *51*, 11867–11871.
- (12) Al-Ghouti, M. A.; Da'ana, D. A. Guidelines for the Use and Interpretation of Adsorption Isotherm Models: A Review. *J. Hazard. Mater.* **2020**, *393*, 122383.
- (13) Foo, K. Y.; Hameed, B. H. Insights into the Modeling of Adsorption Isotherm Systems. *Chem. Eng. J.* **2010**, *156*, 2–10.
- (14) Wang, J.; Guo, X. Adsorption Isotherm Models: Classification, Physical Meaning,

- Application and Solving Method. *Chemosphere* **2020**, 258, 127279.
- (15) Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **1918**, 40, 1361–1403.
- (16) Malek, A.; Farooq, S. Comparison of Isotherm Models for Hydrocarbon Adsorption on Activated Carbon. *AIChE J.* **1996**, 42, 3191–3201.
- (17) Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press, 1998; Vol. 2.
- (18) Sips, R. On the Structure of a Catalyst Surface. *J. Chem. Phys.* **1948**, 16, 490–495.
- (19) Bastos-neto, M.; Azevedo, D. C. S. de; Lucena, S. M. P. de. Adsorption. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, 2020; pp 1–59.
- (20) Shafeeyan, M. S.; Wan Daud, W. M. A.; Shamiri, A. A Review of Mathematical Modeling of Fixed-Bed Columns for Carbon Dioxide Adsorption. *Chem. Eng. Res. Des.* **2014**, 92, 961–988.
- (21) Borba, C. E.; Guirardello, R.; Silva, E. A.; Veit, M. T.; Tavares, C. R. G. Removal of Nickel(II) Ions from Aqueous Solution by Biosorption in a Fixed Bed Column: Experimental and Theoretical Breakthrough Curves. *Biochem. Eng. J.* **2006**, 30, 184–191.
- (22) Al-Janabi, N.; Vakili, R.; Kalumpasut, P.; Gorgojo, P.; Siperstein, F. R.; Fan, X.; McCloskey, P. Velocity Variation Effect in Fixed Bed Columns: A Case Study of CO₂ Capture Using Porous Solid Adsorbents. *AIChE J.* **2018**, 64, 2189–2197.
- (23) Gutiérrez Ortiz, F. J.; Barragán Rodríguez, M.; Yang, R. T. Modeling of Fixed-Bed Columns for Gas Physical Adsorption. *Chem. Eng. J.* **2019**, 378, 121985.
- (24) Sircar, S.; Hufton, J. R. Why Does the Linear Driving Force Model for Adsorption Kinetics Work? *Adsorption* **2000**, 6, 137–147.
- (25) Freitas, F. A. da S. Cyclic Adsorption Process: Application to Propane/Propylene Separation. PhD Thesis, Faculty of Engineering of the University of Porto, 1999.
- (26) Danckwerts, P. V. Continuous Flow Systems. Distribution of Residence Times. *Chem. Eng. Sci.* **1953**, 2, 1–13.

- (27) Fairbanks, D. F.; Wilke, C. R. Diffusion Coefficients in Multicomponent Gas Mixtures. *Ind. Eng. Chem.* **1950**, *42*, 471–475.
- (28) Bird, R. B.; Stewart, W. E.; Lightoot, E. N. *Transport Phenomena*, 2nd Ed.; John Wiley & Sons: New York, 2002.
- (29) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th Ed.; McGraw-Hill, 2001.
- (30) G.Griskey, R.; Fok, S. Y.; Stuewe, C. W. Kihara and Lennard Jones Parameters for the Isomeric Hexanes. *Aiche J.* **1964**, *10*, 584–592.
- (31) Çengel, Y. A.; Boles, M. A. *Thermodynamics an Engineering Approach*, 8th Ed.; McGraw-Hill Education, 2015.
- (32) Reid, R. C.; Sherwood, T. K.; Street, R. E. *The Properties of Gases and Liquids*, 4th Ed.; McGraw-Hill Companies, 1987.
- (33) Votruba, J.; Hlaváček, V.; Marek, M. Packed Bed Axial Thermal Conductivity. *Chem. Eng. Sci.* **1972**, *27*, 1845–1851.
- (34) Wakao, N.; Kaguei, S.; Funazkri, T. Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Heat Transfer Coefficients in Packed Beds. *Chem. Eng. Sci.* **1978**, *34*, 325–336.
- (35) Schiesser, W. E.; Griffiths, G. W. *A Compendium of Partial Differential Equation Models: Method of Lines Analysis with Matlab*; Cambridge University Press, 2009.
- (36) Attaway, S. *MATLAB: A Practical Introduction to Programming and Problem Solving*; Butterworth-Heinemann, 2009.
- (37) Shampine, L. F.; Reichelt, M. W. The MATLAB ODE Suite. *SIAM J. Sci. Comput.* **1997**, *18*, 1–22.
- (38) Lehigh University. wes1's Home Page <https://www.lehigh.edu/~wes1/>.
- (39) Ko, D.; Siriwardane, R.; Biegler, L. T. Optimization of a Pressure-Swing Adsorption Process Using Zeolite 13X for CO₂ Sequestration. *Ind. Eng. Chem. Res.* **2003**, *42*, 339–348.
- (40) Ko, D.; Siriwardane, R.; Biegler, L. T. Optimization of Pressure Swing Adsorption and

- Fractionated Vacuum Pressure Swing Adsorption Processes for CO₂ Capture. *Ind. Eng. Chem. Res.* **2005**, *44*, 8084–8094.
- (41) Zafanelli, L. F. A. S.; Henrique, A.; Karimi, M.; Rodrigues, A. E.; Silva, J. A. C. Single- and Multicomponent Fixed Bed Adsorption of CO₂, CH₄, and N₂ in Binder-Free Beads of 4A Zeolite. *Ind. Eng. Chem. Res.* **2020**, *59*, 13724–13734.
- (42) Fakhroleslam, M.; Fatemi, S. Comparative Simulation Study of PSA, VSA, and TSA Processes for Purification of Methane from CO₂ via SAPO-34 Core-Shell Adsorbent. *Sep. Sci. Technol.* **2016**, *51*, 2326–2338.
- (43) Chai, S. W. Experimental Simulation of Rapid Pressure Swing Adsorption for Medical Oxygen Concentrator and Numerical Simulation of the Critical Desorption-by-Purge Step. PhD Thesis, Lehigh University, 2011.
- (44) Ferreira, D.; Bárcia, P.; Whitley, R. D.; Mendes, A. Single-Stage Vacuum Pressure Swing Adsorption for Producing High-Purity Oxygen from Air. *Ind. Eng. Chem. Res.* **2015**, *54*, 9591–9604.
- (45) Simo, M.; Brown, C. J.; Hlavacek, V. Simulation of Pressure Swing Adsorption in Fuel Ethanol Production Process. *Comput. Chem. Eng.* **2008**, *32*, 1635–1649.
- (46) Silva, F. A. da; Silva, J. A. C.; Rodrigues, A. E. A General Package for the Simulation of Cyclic Adsorption Processes. *Adsorption* **1999**, *5*, 229–244.
- (47) Bárcia, P. S.; Silva, J. A. C.; Rodrigues, A. E. Adsorption Dynamics of C5-C6 Isomeric Fractions in Zeolite Beta for the Octane Improvement of Gasoline. *Energy and Fuels* **2010**, *24*, 1931–1940.

4 PENTANE AND HEXANE ISOMERS SORPTION IN MOF ZIF-8

The content of this chapter is based on:^{1,2}

- (1) Henrique, A.; Rodrigues, A. E.; Silva, J. A. C. Separation of Hexane Isomers in ZIF-8 by Fixed Bed Adsorption. *Ind. Eng. Chem. Res.* **2019**, *58*, 378–394.
- (2) Henrique, A.; Rodrigues, A. E.; Silva, J. A. C. Fixed Bed Dynamics of Single and Multicomponent Adsorption of Pentane and Hexane Isomers in ZIF-8. *Sep. Purif. Technol.* **2020**, *238*, 116419.

The performance of MOF ZIF-8 in the separation of pentane and hexane isomers was evaluated through an extensive series of breakthrough experiments, including single (nC5 and nC6), quinary (nC6/2MP/3MP/23DMB/22DMB and iC5/2MP/3MP/23DMB/22DMB), and septenary (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB) equimolar mixtures. Both single and multicomponent experiments were performed at the temperatures of 373, 423, and 473 K and with total alkane pressure up to 50.0 kPa. Globally, the measured data show the following sorption hierarchy $\text{nC6} > \text{nC5} > 2\text{MP} > 3\text{MP} > \text{iC5} > 23\text{DMB} > 22\text{DMB}$, with the adsorption of linear molecules being dominated by thermodynamic equilibrium in contrast with the branched alkanes, which are kinetically controlled. The septenary breakthrough experiment that includes the pentane isomers, performed at 373 K and 25 kPa, resulted in a selectivity (LRON/HRON molecules) of 23.6 and a 92 RON ideal productivity of $0.176 \text{ mol} \cdot \text{dm}^{-3}$. The quinary experiments dealing with only pentane and hexane branched paraffins evidenced an interesting partial separation by classes of mono- (2MP/3MP/iC5) and di-branched (23DMB/22DMB) alkanes. The Sips isotherm conveniently fitted the adsorption equilibrium, being the simulated breakthrough curves suitably predicted by the dynamic mathematical model, in which kinetic limitation effects are of fundamental importance for the alkane isomers separation. From the fitting of the experimental breakthrough curves, equal k_{LDF} coefficients for linear paraffins (nC5/nC6) were found, ranging from $0.0300 - 0.117 \text{ s}^{-1}$, which are 100 times higher than its corresponding value for the mono-branched alkanes (iC5/2MP/3MP), and 150 and 300 times higher than for the di-branched hexanes 23DMB and 22DMB, respectively. This work shows that ZIF-8 can completely separate the linear from its branched isomers and partially separate mono- from di-branched alkanes if proper experimental conditions are set.

4.1 Introduction

As stated in *Chapter 2*, the ZIF-8 adsorbent represents one of the most extensively investigated MOF for the separation of hexane isomers. However, there is still no complete understanding in using this material for this separation target. Indeed, some authors have a controversial picture, especially if different experimental methods are used to perform the adsorption studies. In static (batch) equilibrium conditions, most of the hexane isomers (except the bulkier 22DMB) are adsorbed in the material,^{3,4} while in continuous fixed bed systems, the linear alkanes nC5 and nC6 are completely separated from their branched counterparts.⁵⁻⁸ These discrepancies are possibly explained due to kinetic considerations related explicitly to fixed bed operating flow conditions, in contrast with static systems, where contact between the gas and the adsorbent has a completely different time scale. Accordingly, the contact time is the one necessary to apparently reach thermodynamic equilibrium.

Despite these divergences, ZIF-8 appears as a very interesting alternative to the industrially used molecular sieve zeolite 5A to separate linear from branched alkanes due to its significantly higher adsorption capacity per mass and also per volume of adsorbent.^{5,6} In addition, two works carried out in flow systems merit attention. Peralta et al.⁵ and Mendes et al.⁶ performed fixed bed breakthrough experiments with equimolar binary mixtures of branched isomers (3MP/22DMB) at similar temperature and pressure working conditions, being the main difference the residence time of the gas mixture in the column, around 20 and 4 s, respectively. The outcomes from Peralta et al. showed a partial separation between them, while in the experiments performed by Mendes et al., no separation was detected, with both branched molecules spontaneously breakthrough at the beginning of the experiment. Apart from being slow diffusion species, according to Zang et al.,⁴ the mono-branched 3MP diffuses three times faster than 23DMB into the pores of the ZIF-8. This might explain why these results are different since, in the experiments performed for Mendes et al., the residence time of the gas in the column was too short not given sufficient time to provide any adsorption of 3MP.

From these observations, it can be presumed that a proper selection of the gas residence time could not only separate linear from branched paraffins, but also give rise to a certain degree of separation between mono- and di-branched alkanes, pointing that a deeper study on this material is required. Moreover, so far, none of the reported experimental works in ZIF-8 show data for the mixtures of all hexane and pentane/hexane isomers that are representative of the conventional TIP process. Therefore, the present chapter aims to better understand the

adsorption of pentane and hexane isomers in ZIF-8 through several fixed bed adsorption experiments. For the first time, experimental breakthrough curves with equimolar quinary mixtures of all hexane isomers and septenary mixtures of pentane and hexane isomers were studied. The influence of temperature, total alkane pressure, and residence time of the gas in the bed were analysed to evaluate the adsorption dynamics behaviour to separate them. With such data, the mathematical model developed in *Chapter 3* was used to identify and clarify the controlling mechanisms of the adsorption process.

The first section of this chapter, Section 4.2, describes the structural and physical properties of the shaped ZIF-8 adsorbent studied by various characterization techniques, including mercury intrusion porosimetry (MIP), N₂ sorption isotherms, and scanning electron microscopy (SEM). In Section 4.3, the experimental and numerical breakthrough results are shown. First, the single component adsorption isotherms of linear components nC5 and nC6 are revealed. Thereafter, a series of experimental breakthrough curves with quinary mixtures of all hexane isomers is described, analysing the effect of the temperature and total alkane pressure. Then, breakthrough curves addressing septenary mixtures of pentane and hexane isomers and quinary mixtures of only branched alkanes are given at a constant total alkane pressure and different temperatures. To give insights into the adsorption dynamics of branched alkanes, their breakthrough curves also explored the effect of the gas residence time in the fixed bed. Afterwards, the equilibrium data is modelled by the Sips isotherm, and fitted parameters used in the dynamic mathematical model, which was systematically explored to interpret and represent the experimental observations, especially with regard to the different k_{LDF} coefficients between linear, mono- and di-branched alkanes. Lastly, a summary of the key findings of the chapter is given in Section 4.4.

4.2 ZIF-8: Material and Characterization

The ZIF-8 material studied in this work was provided by the *Materials Center* of the *Technische Universität Dresden*. It is in the shaped form of small granules randomly oriented with an averaged particle size around to 2 mm, as shown in Figure 4.1. The structural and textural properties of the material were evaluated by a range of characterization techniques, in which its porous nature, surface area, and surface morphology were accessed through MIP, N₂ physisorption isotherms, and SEM analysis, respectively. All characterization studies were performed at the *Laboratorio de Sólidos Porosos* of the *Universidad de Málaga*.

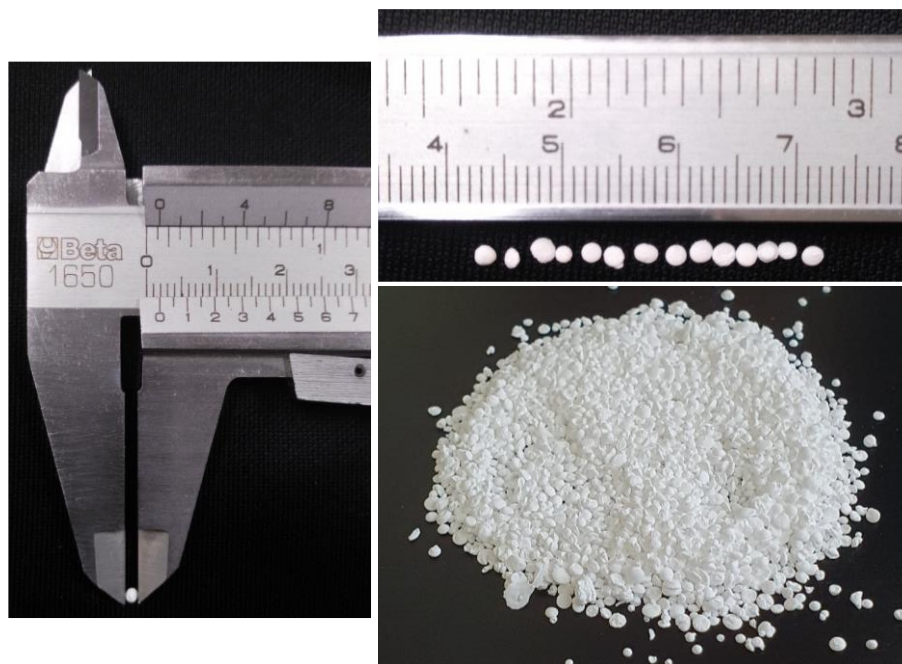


Figure 4.1 | Photo records of ZIF-8 granules.

4.2.1 Porosimetry by Hg Intrusion of ZIF-8

The meso- and macroporosity of the ZIF-8 granules was evaluated by MIP using a pore size analyser (*AutoPore IV 9500, Micromeritics*), applying a contact angle of 130° and covering the pressure range between 3.6×10^{-3} and 2.1×10^2 MPa. Before the experiments, the sample (≈ 120 mg) was outgassed at 423 K for 12 h under a vacuum atmosphere. Figure 4.2 shows the results of the Hg intrusion test. The pore size distribution reveals three types of macropores with sizes centred around 5.0×10^1 , 1.3×10^4 , and 2.3×10^5 nm, which can be interpreted as originating from the intercrystalline pores between the individual ZIF-8 crystals. The curve of the cumulative pore volume indicates a continuous increase in the Hg uptake with a decrease in the pore diameter, i.e., increase of Hg intrusion pressure.

Information on the total intrusion volume, total pore area, median pore diameter (volume and area), average pore diameter ($4V/A$), apparent density, solid density, and porosity is given in Table 4.1. The apparent density of the granulates was determined at the lowest pressure (3.6×10^{-3} MPa), at which Hg does not spontaneously penetrate the pores and only surrounds the particles without wetting them. In contrast, the solid density was obtained at the high pressure (2.1×10^2 MPa), at which Hg is forced into the meso- and macropores (except into the micropores), filling the majority of the secondary pores generated during the shaping process.

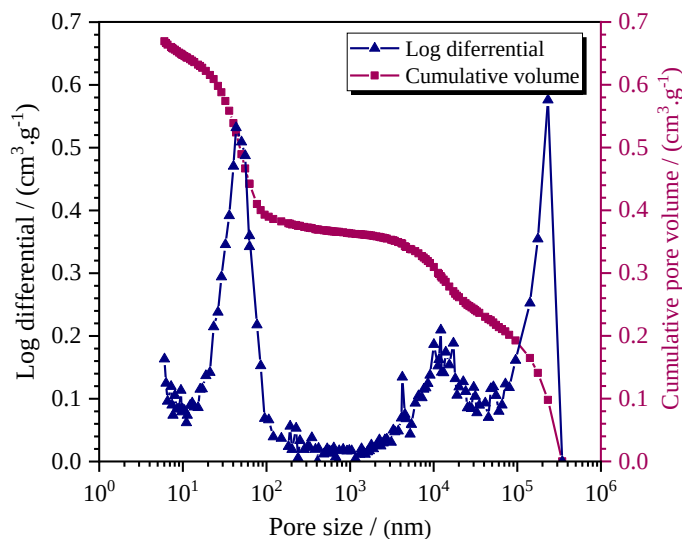


Figure 4.2 | Macroscopic pore size and cumulative pore volume distribution of ZIF-8.

Table 4.1 | Textural properties of ZIF-8 determined by MIP measurements.

Hg porosimetry data		
Total intrusion volume	(cm ³ .g ⁻¹)	0.669
Total pore area	(m ² .g ⁻¹)	41.5
Median pore diameter (volume)	(nm)	6071
Median pore diameter (area)	(nm)	21.9
Average pore diameter (4V/A)	(nm)	64.5
Apparent density	(g.cm ⁻³)	0.325
Solid density	(g.cm ⁻³)	0.914
Porosity	(%)	64.4

4.2.2 N₂ Adsorption and Desorption Isotherms of ZIF-8

Gas sorption measurements were performed to give insight into the surface area of the ZIF-8 material. N₂ adsorption and desorption isotherms were measured in an accelerated surface area and porosimetry system (ASAP® 2420, Micromeritics), at a temperature of 77 K and a pressure range of 2.5 – 10⁵ Pa. Before the experiments, the sample (≈200 mg) was outgassed at 423 K for 12 h under a vacuum atmosphere. The corresponding adsorption equilibrium isotherms are shown in Figure 4.3. As it can be seen, they are of type I according to the updated International Union of Pure and Applied Chemistry (IUPAC) classification,⁹ being concave to the x-axis with the loadings approaching a constant value (horizontal plateau), which is a signature characteristic of microporous materials. The steep uptake at a very low

relative pressure (p/p_0 between 10^{-5} to 10^{-2}) is related to enhanced gas-solid interactions in narrow pores, resulting in pore filling, in which the loading progressively increases up to $\approx 400 \text{ cm}^3 \cdot \text{g}^{-1}$. After filling the micropores, there are no regions where adsorption is significant, and the loading practically remains constant until $p/p_0 = 0.9$, from where a slight increase of N_2 adsorption is seen, suggesting the existence of a small amount of meso- and macropores.

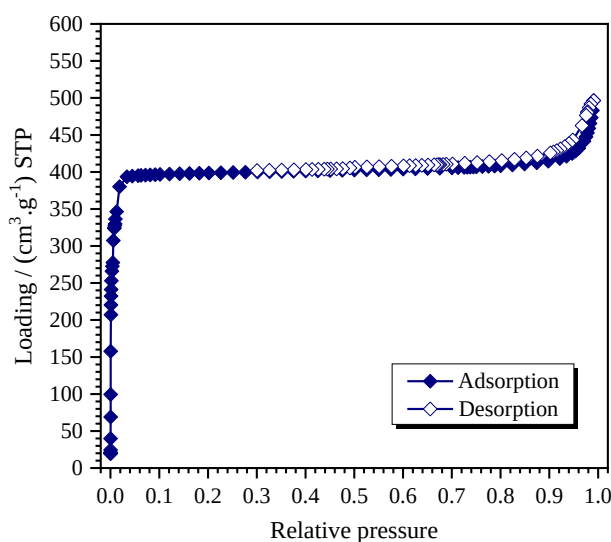


Figure 4.3 | N_2 adsorption and desorption isotherms at 77 K of ZIF-8.

The textural properties of ZIF-8, derived from the N_2 sorption measurements, such as specific surface area (S_{Langmuir}) estimated using the Langmuir method, both external surface area, microporous surface area, and micropore volume determined by the t -method, and the total pore volume calculated at $p/p_0 \approx 0.95$ are summarised in Table 4.2.

Table 4.2 | Textural properties of ZIF-8 determined by N_2 sorption measurements.

N_2 adsorption data		
S_{Langmuir}	$(\text{m}^2 \cdot \text{g}^{-1})$	1743
External surface area	$(\text{m}^2 \cdot \text{g}^{-1})$	23.2
Microporous surface area	$(\text{m}^2 \cdot \text{g}^{-1})$	1719
Micropore volume	$(\text{cm}^3 \cdot \text{g}^{-1})$	0.607
Total pore volume	$(\text{cm}^3 \cdot \text{g}^{-1})$	0.658

4.2.3 SEM Analysis of ZIF-8

To study the surface morphology of ZIF-8, a scanning electron microscopy instrument with high resolution (*JSM-6490, JEOL*) was used. The obtained images showing the characteristic dimension of the granules and their specific crystal appearance at different scales and magnifications are displayed in Figure 4.4. Results confirm that the synthesized ZIF-8 after the shaping is highly crystalline.

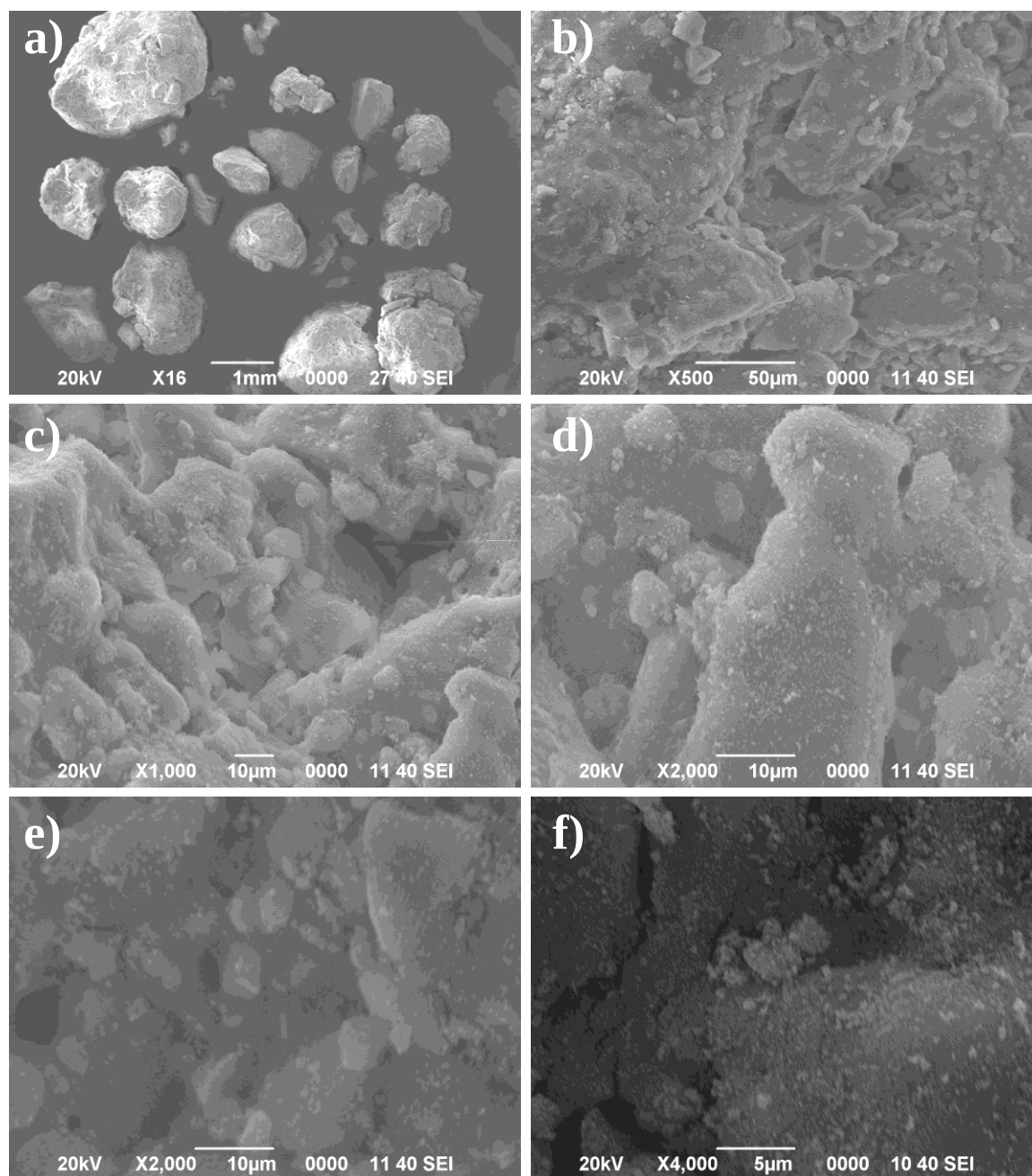


Figure 4.4 | SEM images of ZIF-8 at different scales and magnifications: a) x16, b) x500, c) x1000, d) x2000, e) x2000, and f) x4000.

4.3 Results and Discussion

4.3.1 Single Component Adsorption of Linear Alkanes in ZIF-8

Single component adsorption equilibrium isotherms of linear alkanes nC5 and nC6 in ZIF-8 were determined from breakthrough experiments performed at three different temperatures, 373, 423, and 473 K, and with alkane partial pressure up to 50 kPa. The carrier gas He was used to set a total pressure in the column of 101.3 kPa. Complete information on the experimental fixed bed runs performed, including the flow rates of alkane and He, and also the equilibrium loadings, are summarised in Table 4.3. One can observe that the experimental outcomes are thermodynamically consistent since the equilibrium loadings increase as the alkane partial pressure increase (at a constant temperature) and decrease as the temperature increase (at a constant alkane partial pressure). An overall perspective showing the effect of the temperature in the single component breakthrough curves for nC5 and nC6 can be seen in Figures B.1 and B.2 of *Appendix B*, respectively.

The corresponding adsorption equilibrium isotherms are shown in Figure 4.5, plotted in terms of the loadings as a function of the alkane partial pressure. Note that one experiment means one adsorption equilibrium point in the isotherm. As it shows, at 373 and 423 K, the isotherms for both components are marked type I according to IUPAC classification,⁹ while at 473 K, they approach a linear shape, especially for nC5. In addition, despite having the same kinetic diameter (0.43 nm), the nC6 is the guest molecule that presents a higher affinity with the ZIF-8 material, which is a possible consequence of its longer linear chain that maximizes the interactions with the pore walls.

The isotherms depicted in Figure 4.5 shows that a significant amount of nC6 can be adsorbed in ZIF-8, which goes up to 2.8 mol.kg⁻¹ at 373 K. Moreover, the equilibrium data measured for nC6 is in agreement with the ones reported by Mendes et al.⁶ For instance, at nearly working conditions, 373 K and 10 kPa of alkane partial pressure, they obtained an equilibrium loading of 2.17 mol.kg⁻¹, while in this work, we measured 2.15 mol.kg⁻¹. These observations are helpful to validate the developed screening apparatus (shown in *Chapter 3*). For comparison, at the same conditions, a value of ≈ 1.05 mol.kg⁻¹ was reported by Silva and Rodrigues in pellets of zeolite 5A,¹⁰ which means that the adsorption capacity of ZIF-8 is approximately twice higher.

Table 4.3 | Experimental conditions for measuring single component breakthrough curves of linear alkanes in ZIF-8 and results.

Run	Temp. (K)	Alkane partial pressure (kPa)	Alkane flow rate ($\mu\text{mol}\cdot\text{min}^{-1}$)	He flow rate ($\text{mL}\cdot\text{min}^{-1}$)	Mass of adsorbent (g)	q_i ($\text{mol}\cdot\text{kg}^{-1}$)
<i>Single component: nC5</i>						
1_1	373	11.1	18.2	3.31	1.71	1.45
1_2	373	22.0	36.5	2.94	1.80	2.03
1_3	373	32.5	54.7	2.58	1.80	2.22
1_4	373	42.9	73.0	2.21	1.80	2.34
1_5	373	53.0	91.2	1.84	1.80	2.39
1_6	423	11.1	18.2	3.31	1.80	0.642
1_7	423	22.0	36.5	2.94	1.80	1.06
1_8	423	32.5	54.7	2.58	1.80	1.35
1_9	423	42.9	73.0	2.21	1.80	1.59
1_10	423	53.0	91.2	1.84	1.80	1.75
1_11	473	11.1	18.2	3.31	1.80	0.231
1_12	473	22.0	36.5	2.94	1.80	0.426
1_13	473	32.5	54.7	2.58	1.80	0.603
1_14	473	42.9	73.0	2.21	1.80	0.766
1_15	473	53.0	91.2	1.84	1.80	0.943
<i>Single component: nC6</i>						
2_1	373	10.0	16.2	3.31	1.71	2.15
2_2	373	20.0	32.4	2.94	1.71	2.59
2_3	373	30.0	48.6	2.58	1.71	2.73
2_4	373	40.0	64.8	2.21	1.71	2.79
2_5	373	50.0	81.0	1.84	1.71	2.80
2_6	423	10.0	16.2	3.31	1.71	1.06
2_7	423	20.0	32.4	2.94	1.80	1.75
2_8	423	30.0	48.6	2.58	1.80	1.98
2_9	423	40.0	64.8	2.21	1.71	2.18
2_10	423	50.0	81.0	1.84	1.71	2.21
2_11	473	10.0	16.2	3.31	1.80	0.432
2_12	473	20.0	32.4	2.94	1.80	0.746
2_13	473	30.0	48.6	2.58	1.80	1.07
2_14	473	40.0	64.8	2.21	1.80	1.25
2_15	473	50.0	81.0	1.84	1.80	1.41

The mass of ZIF-8 used in the experiments was packed in column 2 (see Chapter 3);

The flow rates are expressed at the standard temperature and pressure (STP) conditions.

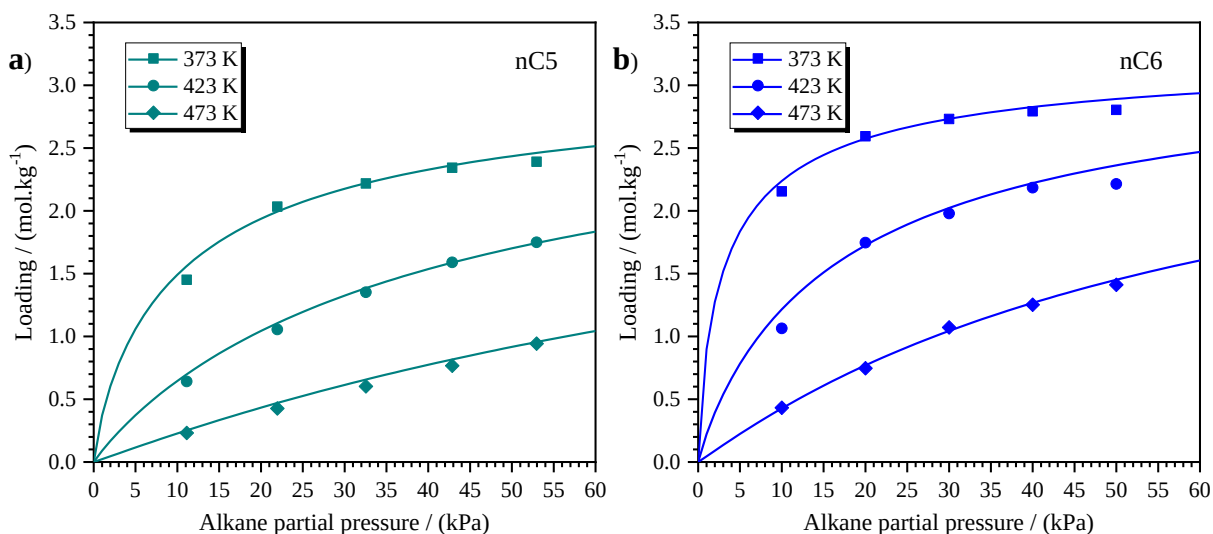


Figure 4.5 | Single component adsorption equilibrium isotherms of linear alkanes in ZIF-8: a) nC5 and b) nC6. The continuous lines represent the Sips model predictions.

4.3.2 Multicomponent Adsorption of Pentane and Hexane isomers in ZIF-8

The adsorption behaviour of pentane and hexane isomers in ZIF-8 was explored by performing a series of multicomponent breakthrough curves with equimolar mixtures. First, the sorption behaviour of all hexane isomers (nC6/2MP/3MP/23DMB/22DMB) is evaluated, in which the effect of the temperature and total alkane pressure is analysed. Thereafter, the pentane isomers were incorporated into the mixture, and breakthrough experiments were carried out with a mixture feed containing all the pentane and hexane isomers (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB) and thereafter only the branched paraffins (iC5/2MP/3MP/23DMB/22DMB). The experiments were conducted in order to ensure a gas residence time in the bed ($\tau = L/v_{int}$) of around 45 s at 373 K, which is approximately twice higher than the one used in the studies performed by Peralta et al.⁵ To complete the breakthrough tests, experiments with pentane and hexane branched alkanes feeds were further performed using different values of gas residence time to assess the influence of this parameter on their adsorption and separation.

4.3.2.1 Multicomponent Adsorption of Hexane isomers

The breakthrough experiments were performed in the same range of temperature and alkane pressure covered in the single component adsorption of linear nC5 and nC6 alkanes. Table 4.4 summarises the experimental conditions applied, the component loadings, the 92

RON ideal productivities, and the selectivities for each run performed. As it shows, the mixture loading follows the same thermodynamic consistency observed in single component experiments.

Figures 4.6, 4.7, and 4.8 show the breakthrough curves for the temperatures of 373, 423, and 473 K, respectively, plotted in terms of the ratio of the normalized molar fraction of each isomer as a function of time. In each figure, the effect of total alkane pressure is shown: a) 10 kPa, b) 25 kPa, and c) 50 kPa. As can be seen, the results indicate that the sorption hierarchy of hexane isomers in ZIF-8 is always $nC6 \gg 2MP > 3MP \gg 23DMB > 22DMB$, being similar to the normal boiling point order of the compounds. However, the profile of the breakthrough curves of linear $nC6$ is very different from the ones observed for the branched paraffins, eluting at a mean retention time different (much higher) than the residence time of the gas in the column. This means that the sorption of $nC6$ is essentially dominated by thermodynamic equilibrium. On the other hand, the branched alkanes start their elution earlier, practically at the residence time of the gas in the column due to strong diffusional limitations. But, their approach to feeding concentration is different since the mono-branched isomers 2MP and 3MP show a wide mass transfer zone due to less diffusion limitations, in contrast with the di-branched ones 23DMB and 22DMB, which rapidly saturate at the early stage of the experiments. As a whole, it can be concluded from all the outcomes that 22DMB is practically excluded from the framework of the ZIF-8, with its counterpart 23DMB showing similar behaviour, in which very small amounts were adsorbed, being the highest loading equal to $0.044 \text{ mol.kg}^{-1}$ obtained at 373 K and 50 kPa.

These observations show that ZIF-8 can completely separate the linear $nC6$ from its branched isomers and partially fractionate mono- and di-branched hexanes in a fixed bed system. Moreover, the experimental sorption hierarchy $nC6 \gg 2MP > 3MP \gg 23DMB > 22DMB$ is for the first time reported, being slightly different from the one predicted by Herm et al.¹¹ from CBMC simulations. Their breakthrough results showed that 2MP started to elute earlier than 3MP (considering equal intra-crystalline diffusion limitations) since this component was assumed to have lower adsorption capacity. However, this is not true, as seen from the breakthrough data shown in Figures 4.6 - 4.8.

Table 4.4 | Experimental conditions for measuring breakthrough curves for equimolar mixtures of pentane and hexane isomers in ZIF-8 and results.

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol.min}^{-1}$)	He flow rate (mL.min^{-1})	q_i (mol.kg^{-1})							q_{mix} (mol.kg^{-1})	P_s RON 92 (mol.dm^{-3})	S_s
					iC5	nC5	22DMB	23DMB	3MP	2MP	nC6			
<i>Quinary mixture (nC6/2MP/3MP/23DMB/22DMB)</i>														
3_1	373	10.0	16.2	3.31	-	-	0.00608	0.0204	0.123	0.210	1.13	1.49	0.0897	55.2
3_2	373	25.0	40.5	2.76	-	-	0.0110	0.0337	0.163	0.270	1.39	1.87	0.134	40.7
3_3	373	50.0	81.0	1.84	-	-	0.0167	0.0442	0.196	0.315	1.58	2.15	0.185	34.3
3_4	423	10.0	16.2	3.31	-	-	0.00408	0.0141	0.0586	0.0978	0.298	0.472	0.0425	25.0
3_5	423	25.0	40.5	2.76	-	-	0.00941	0.0270	0.111	0.186	0.640	0.973	0.114	25.7
3_6	423	50.0	81.0	1.84	-	-	0.0146	0.0384	0.148	0.254	0.864	1.32	0.194	23.9
3_7	473	10.0	16.2	3.31	-	-	0.00341	0.00883	0.0294	0.0497	0.0861	0.177	0.0200	13.5
3_8	473	25.0	40.5	2.76	-	-	0.00744	0.0174	0.0584	0.103	0.193	0.379	0.0592	14.3
3_9	473	50.0	81.0	1.84	-	-	0.0132	0.0324	0.104	0.174	0.357	0.681	0.139	13.9
<i>Septenary mixture (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB)</i>														
4_1	373	25.0	40.5	2.76	0.0563	0.429	0.00568	0.0166	0.121	0.200	1.10	1.93	0.176	23.6
4_2	423	25.0	40.5	2.76	0.0476	0.180	0.00628	0.0150	0.0824	0.139	0.476	0.946	0.107	12.7
4_3	473	25.0	40.5	2.76	0.0364	0.0657	0.00585	0.0136	0.0424	0.0695	0.142	0.375	0.0256	5.71
<i>Quinary mixture (iC5/2MP/3MP/23DMB/22DMB)</i>														
5_1	373	25.0	40.5	2.76	0.0968	-	0.0128	0.0234	0.174	0.276	-	0.584	0.159	3.39
5_2	423	25.0	40.5	2.76	0.0674	-	0.00855	0.0184	0.111	0.164	-	0.369	0.0570	2.91
5_3	473	25.0	40.5	2.76	0.0542	-	0.00691	0.0174	0.0632	0.106	-	0.247	0.0713	2.16

The mass of ZIF-8 used in the experiments was 1.80 g, packed in column 2 (see Chapter 3);

The flow rates are expressed at STP conditions.

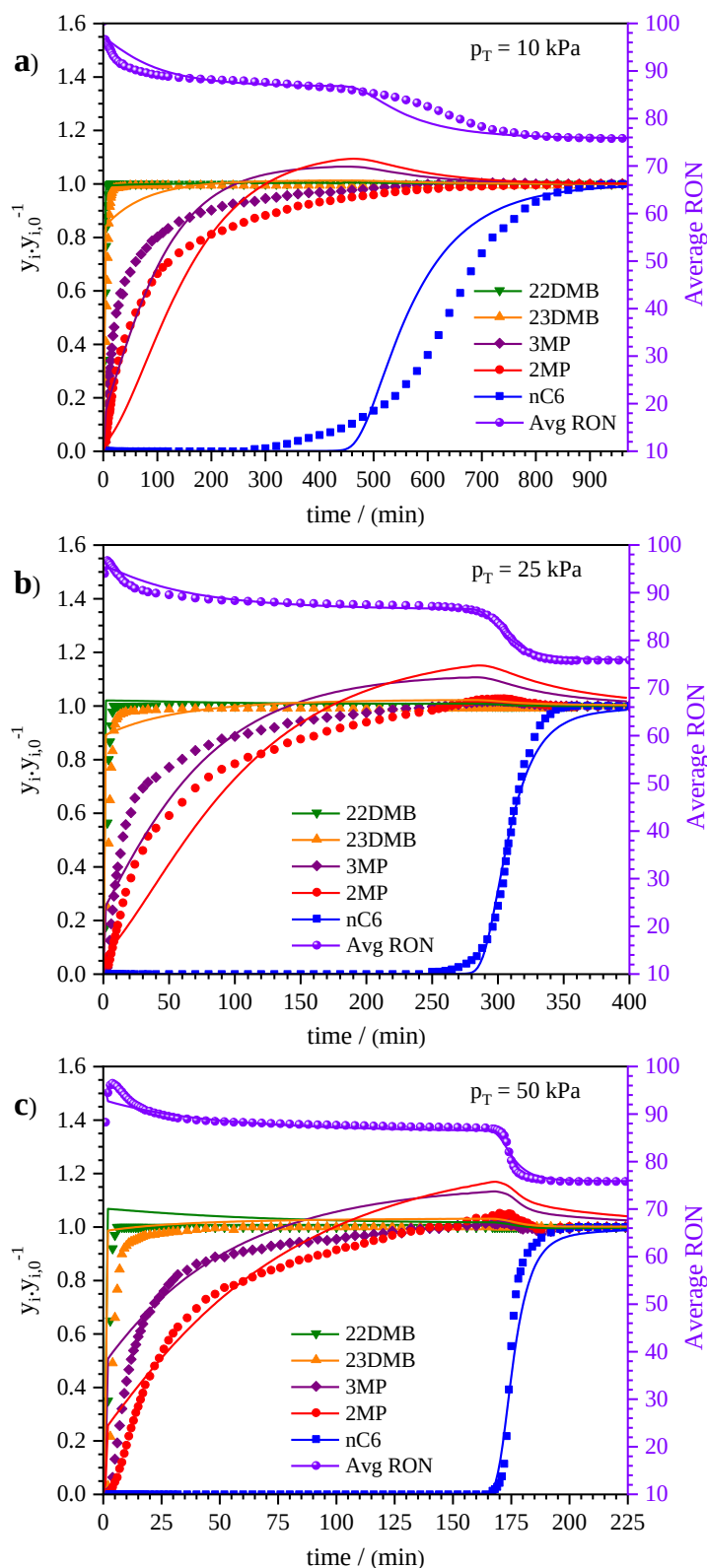


Figure 4.6 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 373 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations. These simulations include diffusional effects with $k_{\text{LDF},\text{nC6}} = 0.0300 \text{ s}^{-1}$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},2\text{MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},3\text{MP}} = 100$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},23\text{DMB}} = 150$ and $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},22\text{DMB}} = 300$.

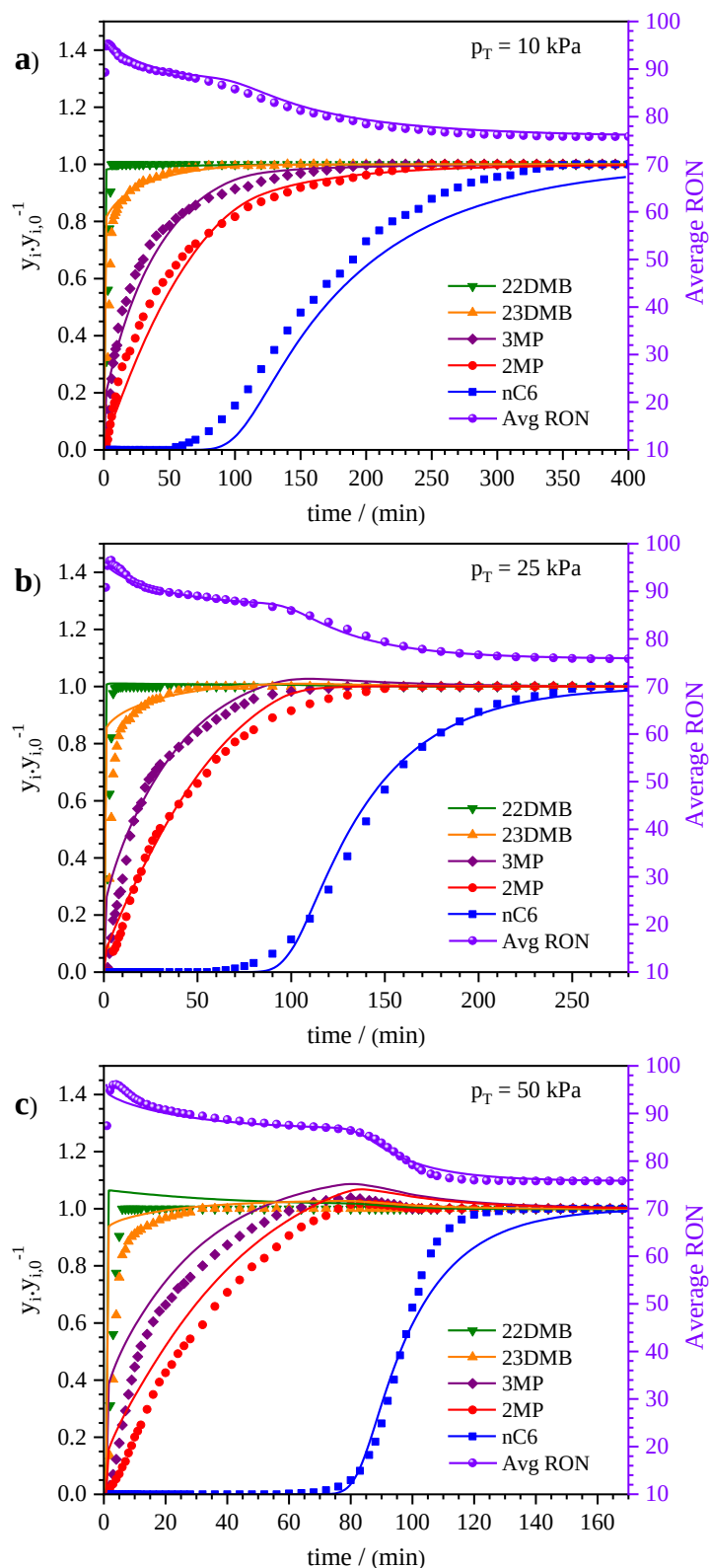


Figure 4.7 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 423 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations. These simulations include diffusional effects with $k_{\text{LDF},\text{nC6}} = 0.0643 \text{ s}^{-1}$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},2\text{MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},3\text{MP}} = 100$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},23\text{DMB}} = 150$ and $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},22\text{DMB}} = 300$.

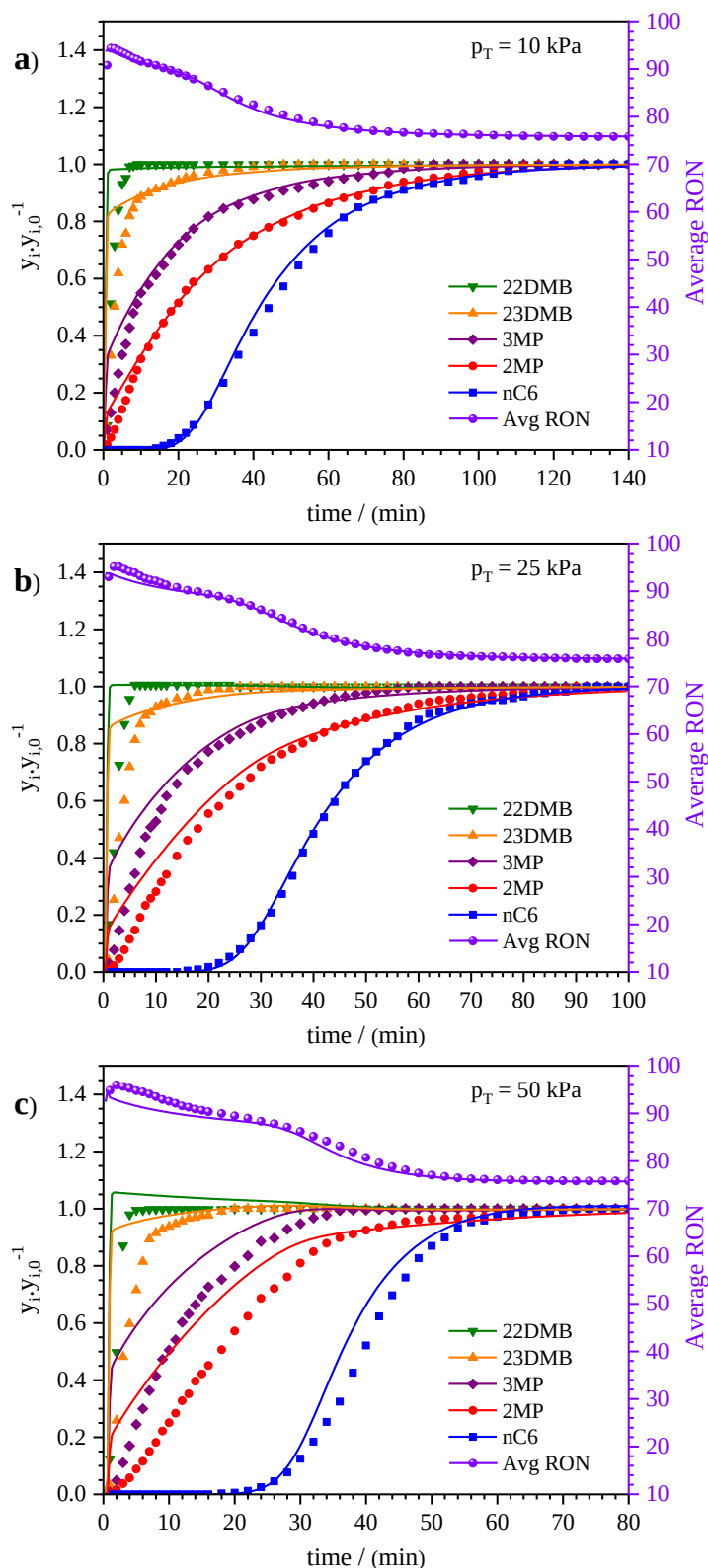


Figure 4.8 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 473 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations. These simulations include diffusional effects with $k_{\text{LDF},\text{nC6}} = 0.117 \text{ s}^{-1}$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},2\text{MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},3\text{MP}} = 100$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},23\text{DMB}} = 150$ and $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},22\text{DMB}} = 300$.

Regarding the effect of the total alkane pressure in the breakthrough curve profiles at each temperature, it is visible in Figures 4.6 - 4.8 the favourable nature of the adsorption equilibrium of nC6, in which its wavefront becomes more sharply as the partial pressure increases. For 2MP and 3MP, it is also shown in Figure 4.6b and c, for the total alkane pressure of 25 and 50 kPa, respectively, an increasing competition for sorption with nC6, with and observed overshoot in concentration near the elution time of the nC6 wavefront. These overshoots are small due to the strong diffusional limitations regarding the sorption of 2MP and 3MP components. The effect of temperature on the concentration profiles of the hexane isomers is also significant. At the highest temperature (473 K, Figure 4.8), the elution time of nC6 is considerably reduced, being closer to the ones of 2MP and 3MP, where nC6 approaches the inlet concentration practically at the same time as them. This is due to the decreasing selectivity with increasing temperature between linear and mono-branched isomers.

The real-time RON of the product mixture leaving the column is also plotted in the figures (right y-axis). Values higher than 95 can be read at the very beginning of the experiments, in which the fraction of branched paraffins eluting from the column is practically composed of only di-branched 23DMB and 22DMB. Additionally, at the lowest temperature of 373 K (Figure 4.6), after their complete elution, the RON values decrease to 88 due to the breakthrough of the mono-branched 2MP and 3MP, and a plateau is reached until linear nC6 leaves the column. Thereafter, the bed is completely saturated with no further changes in the outlet compositions of the compounds. As the temperature increases, this plateau progressively disappears due to its strong impact on the elution time of nC6.

The 92 RON ideal productivities (Eq. 3.4, *Chapter 3*) calculated using the apparent density of ZIF-8 granules, 0.325 g.cm^{-3} (Table 4.1), generally decrease with temperature and increase with total alkane pressure. At 423 K and 50 kPa, a value of $0.194 \text{ mol.dm}^{-3}$ is obtained. It should be noted that the very small value of the apparent particle density of ZIF-8 significantly decreases the ideal productivity on a volume basis of this material (a third of the gravimetric one), which can be a considerable drawback for its use in industrial applications.

The sorption selectivities for the hexane isomers, calculated using the ratio of the loadings between linear + mono-branched paraffins over the di-branched ones (Eq. 3.5, *Chapter 3*), are given as a function of total alkane pressure in Figure 4.9. Globally, they decrease with increasing temperature. A substantial value of approximately 55 is found at 373 K and 10 kPa, decreasing to 35 at 50 kPa. In addition, at the temperatures of 423 and 473 K, the total alkane pressure has almost no effect on selectivity, in which they practically remain constant. Another

remark is that the selectivity is significantly higher at the lowest temperature, mainly because the nC6 adsorption progressively decreases with temperature increasing. It is noteworthy that these selectivities can be, in a certain way, controversial because not all compounds adsorb in ZIF-8 by a similar mechanism (thermodynamic or kinetic), and therefore the definition of selectivity could not be the same. However, since the sorption behaviour is a mix of both mechanisms, it is difficult to define a proper correlation. We believe that the reported values based on equilibrium give an indication about the performance capability of ZIF-8 to separate the hexane isomers in a fixed bed adsorber.

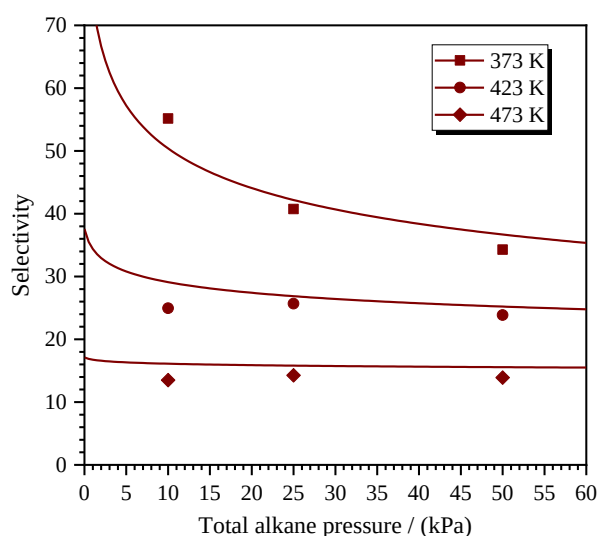


Figure 4.9 | Sorption selectivities of hexane isomers in ZIF-8. The continuous lines represent the Sips model predictions.

Figure 4.10 gathers the quinary adsorption isotherms of hexane isomers in ZIF-8. It is important to highlight that the loading capacities of branched paraffins should be read with caution since they are valid for the working conditions selected in this set of experiments (particularly the residence time of the gas in the bed). As it shows, the component loadings are separated based on their class, linear (nC6) > mono-branched (2MP/3MP) > di-branched (23DMB/22DMB) isomers, especially at 373 and 423 K. In addition, it can also be observed for nC6, which sorption is totally equilibrium based, that the isotherms follow the same classification observed in the single component experiments. They are marked as type I at 373 and 423 K, and approach a linear shape at 473 K.

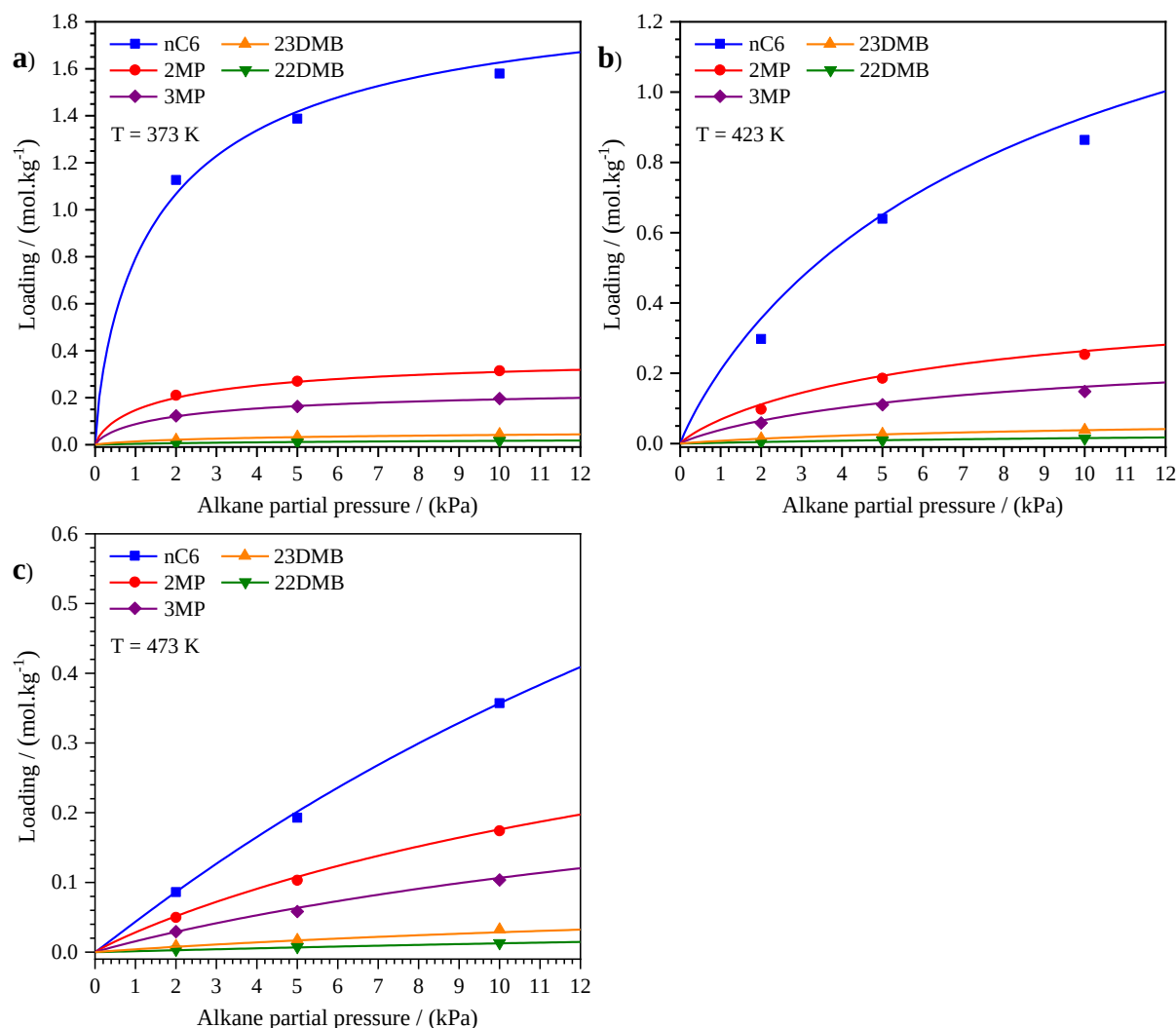


Figure 4.10 | Quinary adsorption equilibrium isotherms of hexane isomers in ZIF-8: a) 373 K, b) 423 K, and c) 473 K. The continuous lines represent the Sips model predictions.

4.3.2.2 Multicomponent Adsorption of Pentane and Hexane Isomers

The screening tests considering septenary mixtures of pentane and hexane isomers were performed at a total alkane pressure of 25 kPa and temperatures of 373, 423, and 473 K (Figure 4.11, panels a), b), and c), respectively). Information on the experimental conditions and results are also given in Table 4.4.

Results indicate that the sorption hierarchy is always $\text{nC6} > \text{nC5} \gg 2\text{MP} > 3\text{MP} > \text{iC5} > 23\text{DMB} > 22\text{DMB}$. As expected, the dynamic behaviour of pentane isomers follows the same trend observed on the hexane breakthrough curves, with the sorption of the linear nC5 being dominated by equilibrium, while for the mono-branched iC5 is kinetically controlled. An interesting remark observed in Figure 4.11a is the overshoot of nC5 at the elution time of the

nC6 wavefront, being its concentration almost 50% higher than the one in the feed of the column. This is evidence that strong interactions occur in ZIF-8 due to competitive adsorption with nC6. When the temperature increases (Figure 4.11b and c), this overshoot in concentration is significantly reduced since the loadings and respective interactions occurring inside the material become smaller.

The ability of ZIF-8 to separate pentanes and hexane mixtures has been widely studied by several authors separately, but none addressed mixtures of all the components. Here, such a study reported in Figure 4.11a shows that the linear paraffins nC5 and nC6 are completely separated from their branched isomers, and the mono-branched alkanes 2MP, 3MP, and iC5 are partially separated from the di-branched hexanes 23DMB and 22DMB. At the beginning of the experiment, the RON values go up to 95, mainly associated with the rapid elution of 23DMB and 22 DMB due to their strong diffusional limitations. The 92 RON ideal productivity resulted in $0.176 \text{ mol.dm}^{-3}$, which is higher than the previously reported for the adsorption of only hexane isomers at the same working conditions (run3_2, $0.134 \text{ mol.dm}^{-3}$). This is due to the similar time elution of the HRON iC5 (RON 92.3), which leaves the column partially mixed with 23DMB and 22DMB, increasing the time in which the product gas mixture has an average RON of 92. Moreover, the selectivity for this experimental run is equal to 23.6.

When the temperature increases in the fixed bed (Figure 4.11b and c), the degree of separation by classes of branching decreases. The mono-branched fraction becomes to be mixed with the linear nC5, which reduces elution time, interestingly overcoming its approach to the inlet concentration (saturation) first than 2MP and 3MP. In this way, the partial separation of mono and di-branched alkanes is also affected, where at 473 K, the maximum RON value read is approximately 92.8, and the selectivity is reduced to 5.71.

Another critical observation that can be retained from these experiments is that at the higher temperatures of 423 and 473 K, the HRON iC5 (RON 92.3) has an elution time closer to the fraction of LRON 2MP (RON 73.4) and 3MP (RON 74.5) hexanes, which represents a drawback given the octane improvement of gasoline. An improved adsorptive fractionating process would selectively isolate the most valuable paraffins 23DMB/22DMB/iC5 from the other LRON alkanes.

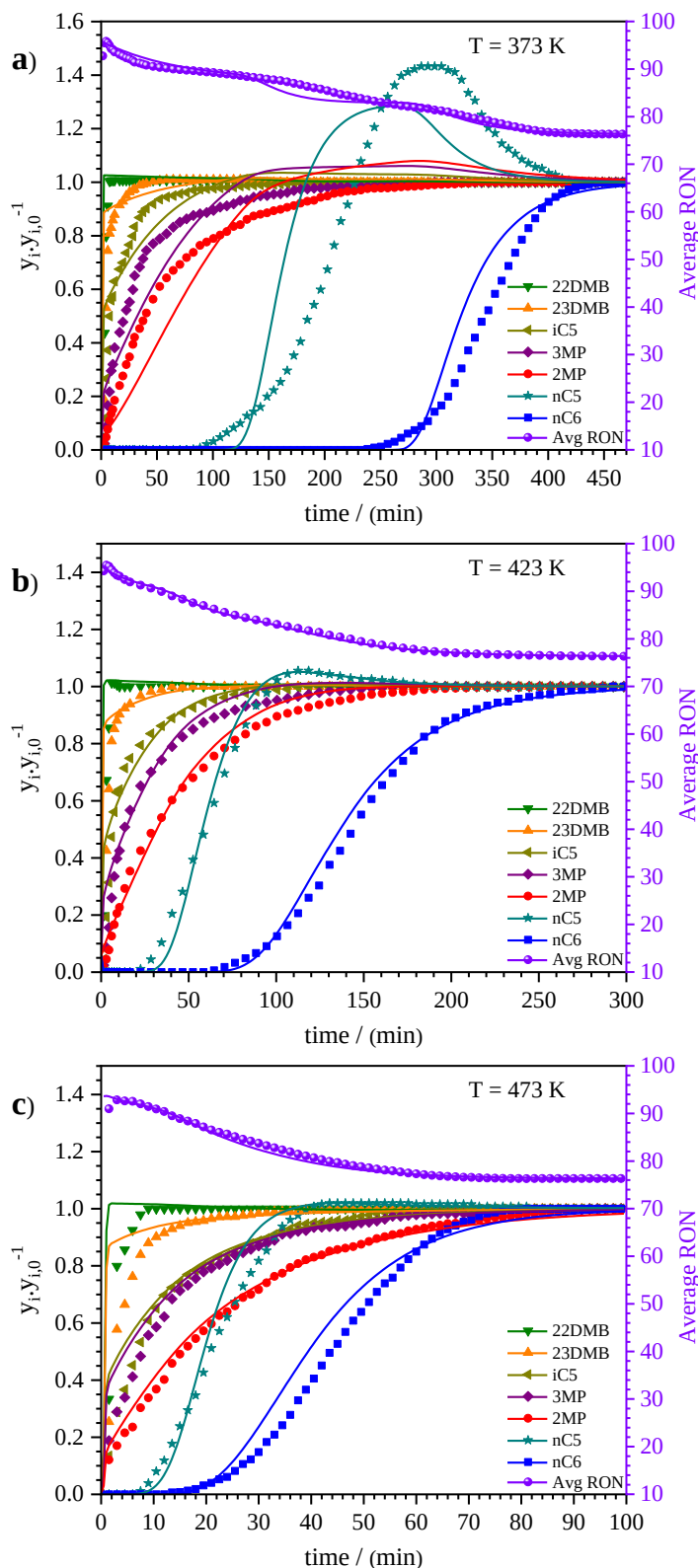


Figure 4.11 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in ZIF-8 at 25 kPa: a) 373 K, b) 423 K, and c) 473 K. The continuous lines represent the numerical simulations. These simulations include diffusional effects with $k_{\text{LDF},\text{nC6}} = k_{\text{LDF},\text{nC5}} = 0.0300 \text{ s}^{-1}$ (at 373 K), 0.0643 s^{-1} (at 423 K), 0.117 s^{-1} (at 473 K), $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{2MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{3MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{iC5}} = 100$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{23DMB}} = 150$ and $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{22DMB}} = 300$.

4.3.2.3 *Multicomponent Adsorption of Pentane and Hexane Branched Alkanes*

In light of the previous septenary experiments results and in order to check the adsorption behaviour of ZIF-8 without the presence of the linear paraffins, screening tests considering only branched alkanes were performed at the same working conditions, see Table 4.4. The breakthrough curves are shown in Figure 4.12 (panels a), b) and c)), from where it can be seen the same sorption hierarchy previously observed, it being $2MP > 3MP > iC5 > 23DMB > 22DMB$. In addition, this figure also shows that, for the selected gas residence time used in this work, it is not feasible to obtain a complete separation between mono- and di-branched alkanes since both fractions start eluting at the residence time of the gas in the column. This means that the fraction of di-branched isomers will always be contaminated with mono-branched ones.

It can also be concluded from Figure 4.12 that removing the linear paraffins from the feed mixture does not significantly impact the sorption behaviour of the branched alkanes. For instance, at 373 K, the obtained 92 RON ideal productivity is equal to $0.159 \text{ mol.dm}^{-3}$, slightly lower than the one obtained with all seven components (run 4_1, $0.176 \text{ mol.dm}^{-3}$).

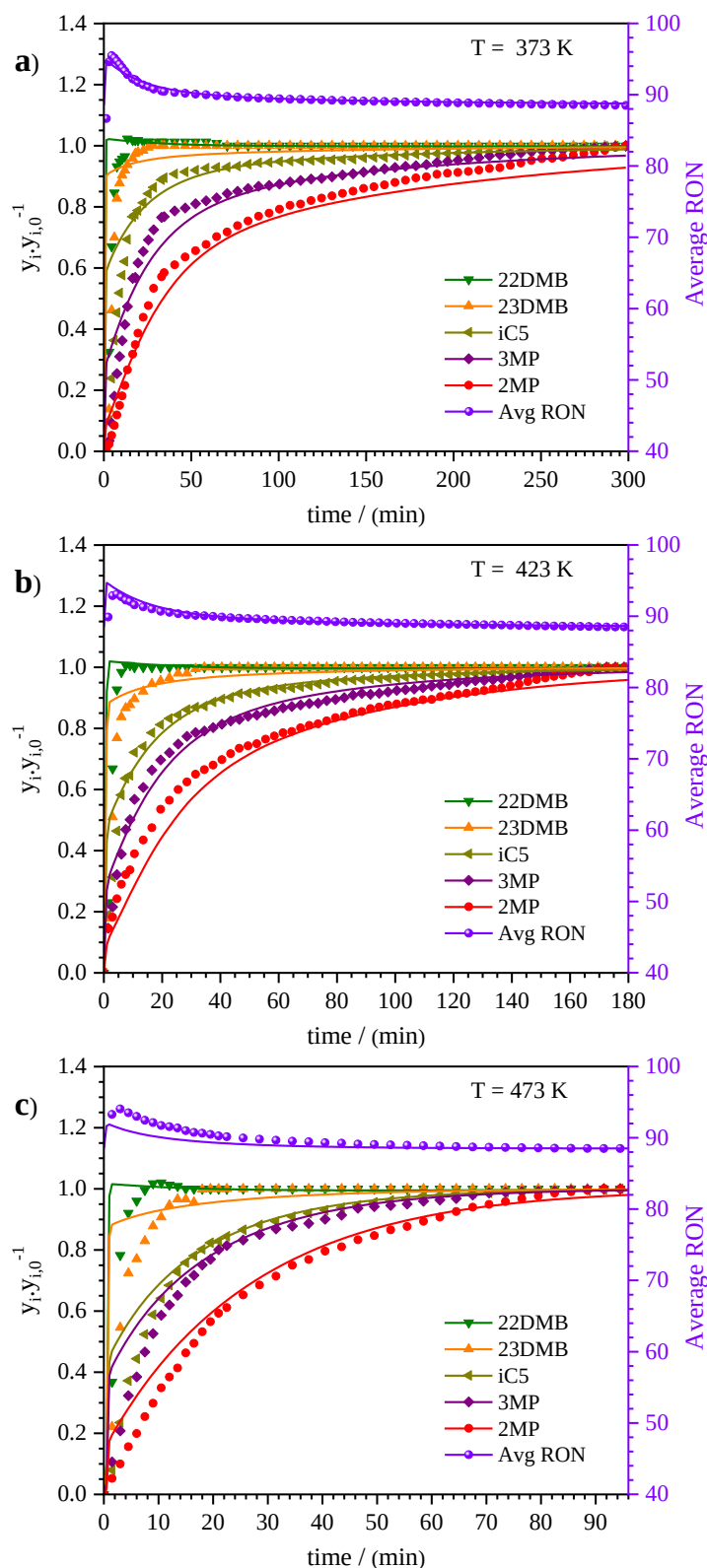


Figure 4.12 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of pentane and hexane branched alkanes in ZIF-8 at 25 kPa: a) 373 K, b) 423 K, and c) 473 K. The continuous lines represent the numerical simulations. These simulations include diffusional effects with $k_{\text{LDF},\text{nC6}} = k_{\text{LDF},\text{nC5}} = 0.0300 \text{ s}^{-1}$ (at 373 K), 0.0643 s^{-1} (at 423 K), 0.117 s^{-1} (at 473 K), $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},2\text{MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},3\text{MP}} = k_{\text{LDF},\text{nC6}}/k_{\text{LDF},\text{iC5}} = 100$, $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},23\text{DMB}} = 150$ and $k_{\text{LDF},\text{nC6}}/k_{\text{LDF},22\text{DMB}} = 300$.

4.3.2.4 *Influence of the Gas Residence Time on the Adsorption Behaviour of Pentane and Hexane Branched Alkanes*

Since the adsorption of pentane and hexane branched alkanes in ZIF-8 is kinetically controlled, the contact time between the gas mixture and the adsorbent inside the column is a parameter of extreme importance. Due to the very slow diffusion of the branched alkanes, especially 22DMB and 23DMB, a considerable degree of separation between mono- from di-branched alkanes can be achieved if this parameter is correctly set up. Therefore, to analyse the effect of this parameter, breakthrough adsorption experiments were performed at 423 K and 25 kPa using three different τ : 22, 40, and 79 s. The experimental conditions, as well as the calculated loadings, are reported in Table 4.5, and the breakthrough curves are shown in Figure 4.13 (panels a), b), and c), respectively). For a direct comparison, the ratio of the normalized molar fraction of each alkane is plotted as a function of its molar amount fed to the column per unit mass of adsorbent. Thus, the x-axis is represented by the following equation:

$$\frac{tF_i}{m_s} = \left[\frac{\text{min mol}_i}{\text{kg min}} \right] = \left[\frac{\text{mol}_i}{\text{kg}} \right] \quad (4.1)$$

Table 4.5 | Experimental conditions for measuring breakthrough curves for a quinary equimolar mixture of pentane and hexane branched alkanes in ZIF-8 at different gas residence times and results.

Run	τ (s)	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol}.\text{min}^{-1}$)	He flow rate ($\text{mL}.\text{min}^{-1}$)	q_i ($\text{mol}.\text{kg}^{-1}$)					q_{mix} ($\text{mol}.\text{kg}^{-1}$)
						iC5	22DMB	23DMB	3MP	2MP	
6_1	22	423	25.0	73.4	5.00	0.0545	-	0.0121	0.0895	0.148	0.304
6_2	40	423	25.0	40.5	2.76	0.0674	0.00855	0.0184	0.111	0.164	0.369
6_3	79	423	25.0	20.3	1.38	0.0860	0.0130	0.0393	0.132	0.205	0.475

The mass of ZIF-8 used in the experiments was 1.80 g, packed in column 2 (see Chapter 3);

The flow rates are expressed at STP conditions.

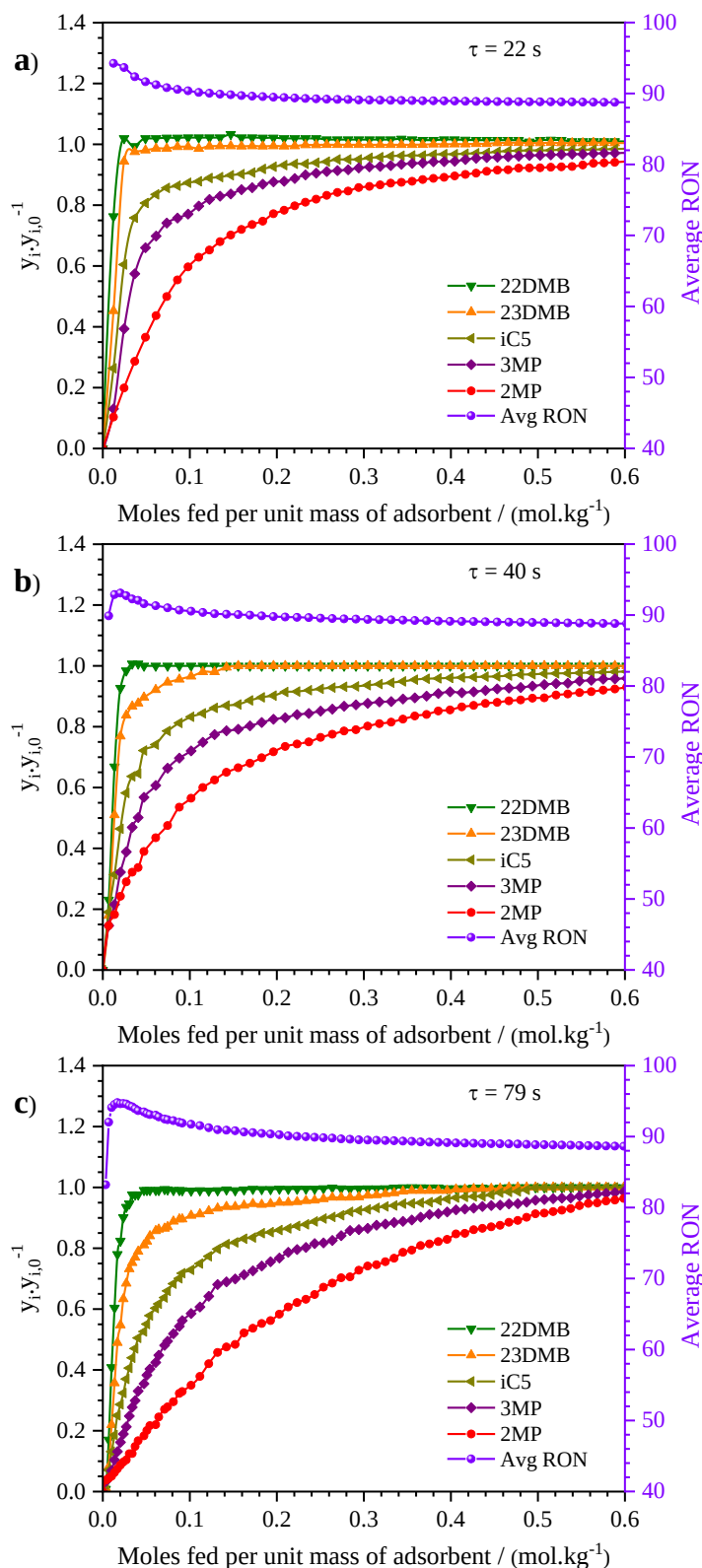


Figure 4.13 | Experimental breakthrough curves for a quinary equimolar mixture of pentane and hexane branched alkanes in ZIF-8 at 423 K, 25 kPa, and different gas residence times: a) 22 s, b) 40 s, and c) 79 s.

At the lowest τ (22 s, Figure 4.13a), 22DMB and 23DMB are practically excluded from the fixed bed, in which they spontaneously come out and saturate since the time spent inside the column is shorter than the one needed to diffuse into the pores of the material. When the contact time increases (Figure 4.13b and c), it is clear that apart from starting eluting nearly at τ , their approach to saturation is delayed, meaning that they are being adsorbed in the bed with an increase in their mass transfer zone. For example, at τ of 79 s (Figure 4.13c), the saturation of 23 DMB is reached only after a feed of 0.4 mol.kg^{-1} . Similar analysis can be observed for the other compounds. Fixing a feed value of 0.2 mol.kg^{-1} , we can observe that the breakthrough curve shows a concentration of 2MP that is 60% of the inlet at a τ of 79 s (Figure 4.13c), which compares to a value of 80% at a τ of 22 s (Figure 4.13a). This behaviour results in different loadings, as can be read in Table 4.5. Accordingly, the calculated loadings for the mono-branched alkanes at τ of 79 s are around 30% higher than at τ of 22 s. Moreover, the experiment performed at the longest τ resulted in a 92 RON ideal productivity twice higher ($0.172 \text{ mol.dm}^{-3}$) than that obtained at τ of 22 s ($0.0839 \text{ mol.dm}^{-3}$). This augmentation directly relates to the increasing adsorption of 3MP and 2MP hexanes, which extends the time in which the product gas mixture leaves the column with an average RON of 92.

These experiments clearly show that the gas residence time strongly affects the sorption dynamics of branched alkanes in ZIF-8, in which the higher the contact time between gas mixture and material, the higher the adsorption of the branched alkanes. Moreover, they also confirm why the experiments performed by Mendes et al.⁶ resulted in a complete exclusion of all branched paraffins from the fixed bed, where spontaneous breakthrough curves were obtained in a τ of approximately 4 s. This is an important observation that can be exploited for the separation of pentane and hexane isomers in industrial operations under flow conditions. However, severely difficult the laboratory and respective characterization study of the material.

4.3.3 Modelling Adsorption Equilibrium Isotherms

The fitting results for the single component isotherms of linear alkanes and multicomponent quinary isotherms of hexane isomers in ZIF-8 have already been shown in Figures 4.5 and 4.10 by the continuous lines, respectively. As demonstrated, a reasonable agreement between model and experimental data was observed. For the fitting procedure, the loadings obtained from the single (Table 4.3) and multicomponent (Table 4.4) breakthrough experiments performed under a gas residence time of 45 s were correlated with the Sips

isotherm model described in *Chapter 3*. One can also note that the selectivities predicted by the model in Figure 4.9 show similar behaviour to the experimental ones.

In addition, it is essential to highlight that the modelled isotherms for nC5 and nC6 can be assumed as the representative of the system since they were obtained from breakthrough curves measured under equilibrium conditions. On the other hand, the modelled isotherms for the branched paraffins may not represent the true adsorption equilibrium in ZIF-8 as measured in a static system and can only apply to the present system studied. Therefore, the equilibrium data reported here for 22DMB, 23DMB, iC5, 3MP, and 2MP may be considered as pseudo adsorption equilibrium isotherms since as the residence time of the gas changes, the loadings also change, as can be observed in Figure 4.13 and Table 4.5. However, it is possible to ensure that for a flow system with a gas residence time of 45 seconds with similarly sized particles of ZIF-8, the data can be assumed as accurate, since several adsorption/desorption cycles were performed and results obtained were the same, meaning that there is no mass accumulation inside the particles. The corresponding model parameters obtained from the fitting procedure are reported in Table 4.6.

Table 4.6 | Sips isotherm parameters for the sorption of pentane and hexane isomers in ZIF-8 and average deviation between model predictions and experimental data.

Sips Parameters		Pentane isomers		Hexane isomers			
		nC5	iC5	nC6	2MP	3MP	23DMB 22DMB
$q_{sat,i}$	(mol.kg ⁻¹)	3.15	1.10	3.30	2.50	2.30	0.950 0.750
$-\Delta H_i$	(kJ.mol ⁻¹)	34.4	22.3	41.6	25.2	23.0	21.0 17.8
$n_{0,i}^*$	(-)	1.21	1.29	1.33	1.31	1.28	1.09 0.928
α_i	(-)	0.971	0.198	1.34	0.722	0.829	0.250 0.133
<i>Temperature: 373 K</i>							
$n_{1,i}$	(-)	1.21	1.29	1.33	1.31	1.28	1.09 0.928
$b_{1,i}$	(kPa ⁻¹)	0.0880	0.0250	0.270	0.0435	0.0270	0.0160 0.0111
<i>Temperature: 423 K</i>							
$n_{2,i}$	(-)	1.06	1.25	1.10	1.18	1.14	1.06 0.914
$b_{2,i}$	(kPa ⁻¹)	0.0237	0.0107	0.0553	0.0166	0.0112	0.00718 0.00565
<i>Temperature: 473 K</i>							
$n_{3,i}$	(-)	0.968	1.22	0.967	1.09	1.04	1.03 0.904
$b_{3,i}$	(kPa ⁻¹)	0.00844	0.00549	0.0158	0.00780	0.00564	0.00382 0.00331
$\Sigma \bar{\Delta}q$		0.0168					

* The reference temperature used was $T_0 = 373$ K.

As indicated in the table, q_{sat} , b , and ΔH (magnitude) follow the same sorption hierarchy order observed in the breakthrough curves: nC6 > nC5 > 2MP > 3MP > iC5 > 23DMB > 22DMB. In addition, it is also specified that the heterogeneity parameter n decreases with temperature for all components, suggesting that the heterogeneity of the system is apparently smaller as the temperature increases.

Data can be compared with literature for nC6, whose sorption behaviour is equilibrium-based. The q_{sat} obtained in this work is equal to 3.3 mol.kg⁻¹, being similar to the one found by Mendes et al.⁶ (3.13 mol.kg⁻¹) and slightly higher than that from Ferreira et al.³ (2.70 mol.kg⁻¹). In addition, the constant b lies between 0.270 kPa⁻¹ (373 K) to 0.0158 kPa⁻¹ (473 K), where the value obtained at 373 K compares to the one reported by Mendes et al. (0.284 kPa⁻¹) and is lower than that from Ferreira et al. (0.40 kPa⁻¹). Regarding the $-\Delta H$, a value around 41.6 kJ.mol⁻¹ is reported on Table 4.6, reflecting the strong impact of the temperature on the adsorption of nC6, which was also stated by Ferreira et al. (41.4 kJ.mol⁻¹),

being higher than the one estimated by Mendes et al. (32.8 kJ.mol⁻¹). We should specify that both works fitted their experimental data with the Langmuir isotherm model.

Figure 4.14 shows the single component isotherms for the nC6 predicted by the Sips and Langmuir models at similar working conditions. It can be observed that the isotherms predicted in this work are very similar to those reported by Mendes et al. at both temperatures (373 and 473 K). Comparing our results with Ferreira et al., at lower alkane partial pressures, up to approximately 10 kPa, the isotherms are in close agreement.

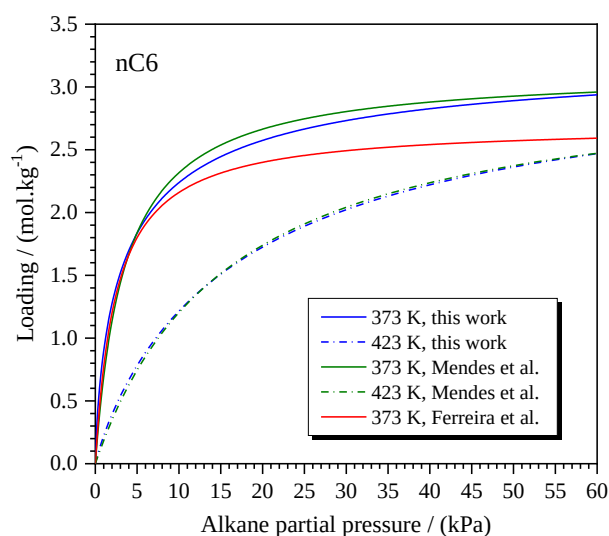


Figure 4.14 | Single component adsorption equilibrium isotherms of linear nC6 in ZIF-8. Literature comparison between model predictions.

In adsorption equilibrium studies, it is also important to obtain data about adsorption heats. For the Sips isotherm model, the evolution of the isosteric heat of adsorption, Q , as a function of coverage, can be calculated accordingly:¹²

$$(-Q) = \Delta H - (\alpha RT_0)n^2 \ln\left(\frac{q}{q_{sat} - q}\right) \quad (4.2)$$

The correlation is obtained from the van't Hoff equation and taking the total derivative of the Sips isotherm, considering that q_{sat} is invariant with temperature. Besides its dependence on the loading, Eq. 4.2 is also a function of temperature, reflecting the dependence of the parameters b and n .

Figure 4.15 shows the pattern of the Q for nC5 and nC6 as a function of their fractional coverage ($\theta = q/q_{sat}$), determined using the isotherms fitted to the experimental data. As can

be seen, Q decreases as pressure increases, i.e., with loading, and when θ reaches 0.5, the value of Q is equal to $-\Delta H$, at all temperatures, which is a characteristic of the Sips equation.

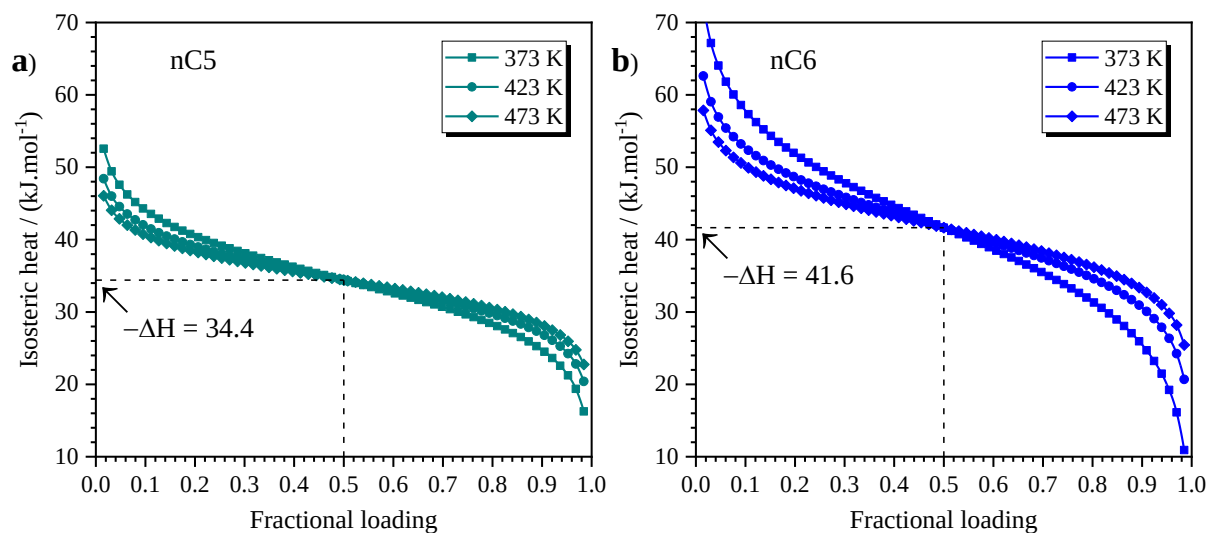


Figure 4.15 | Isosteric heat of linear alkanes in ZIF-8 predicted by the Sips isotherm: a) nC5 and b) nC6.

4.3.4 Numerical Simulations of Single and Multicomponent Breakthrough Curves

Since the adsorption of linear paraffins in ZIF-8 is essentially equilibrium based, the simulations for the single component breakthrough curves were conducted ensuring weak diffusional limitations. From the fitting procedure, equal k_{LDF} coefficients for nC5 and nC6 were found (Eq. 3.22, *Chapter 3*), ranging from 0.0300 s^{-1} (373 K) to 0.117 s^{-1} (473 K). Globally, it can be seen that a good agreement between numerical predictions and experimental data is observed, with the model capturing the shape of the breakthrough curves (Figures B.1 and B.2, respectively).

For the multicomponent experiments, the simulations were performed in two ways: 1) accounting for strong diffusional resistances (low diffusivities) for branched paraffins (Figures 4.6 - 4.8, 4.11, and 4.12), and 2) assuming weak diffusional resistances and equal for all components (high diffusivities). The differences between the mass transfer coefficients of the alkane isomers in panel 1 are accounted by different ratios ($k_{LDF,nC6}/k_{LDF,nC5}$), ($k_{LDF,nC6}/k_{LDF,iC5}$), ($k_{LDF,nC6}/k_{LDF,2MP}$), ($k_{LDF,nC6}/k_{LDF,3MP}$), ($k_{LDF,nC6}/k_{LDF,23DMB}$), and ($k_{LDF,nC6}/k_{LDF,22DMB}$), while in Figure B.3, it is shown the scenario when these ratios are equal to 1 (panel 2).

As a starting point for the simulations considering low diffusivities, we selected the diffusional ratios reported by Herm et al.,¹¹ calculated from CBMC predictions regarding the sorption of hexane isomers in ZIF-8 at 433 K, see Table 4.7. From there, the best ratios to properly match the experimental data were established and also summarised in the Table 4.7 for comparison. As it can be seen, in the present experimental study, the diffusion time constant of nC6 is approximately twice lower than the one estimated by CBMC. For the branched isomers, the ratios $k_{LDF,nC6}/k_{LDF,2MP}$ and $k_{LDF,nC6}/k_{LDF,3MP}$ are the same, while the $k_{LDF,nC6}/k_{LDF,23DMB}$ is twice lower than the $k_{LDF,nC6}/k_{LDF,22DMB}$ ratio. This means that the diffusivity of branched paraffins in ZIF-8 is two orders of magnitude lower than for the linear ones and that the diffusivity of di-branched alkanes is up to three times lower than that for its mono-branched counterparts. Therefore, the values obtained in this work validate in a certain way the CBMC results from Herm et al. The temperature dependence of the diffusivities, calculated from the Arrhenius equation (Eq. 3.23, *Chapter 3*), gave rise to an ΔE_i of 20 kJ.mol⁻¹ for all alkane isomers. In addition, the simulations revealed that the system is isothermal.

Table 4.7 | Diffusional ratios for the sorption of pentane and hexane isomers in ZIF-8.

Diffusivity Ratios	Herm et al. ¹¹	This work
D_{nC6}/r^{2**}	0.00833 s ⁻¹	0.00488 s ⁻¹
$k_{LDF,nC6}/k_{LDF,nC5}$	-	1.00
$k_{LDF,nC6}/k_{LDF,2MP}$	100	100
$k_{LDF,nC6}/k_{LDF,3MP}$	100	100
$k_{LDF,nC6}/k_{LDF,iC5}$	-	100
$k_{LDF,nC6}/k_{LDF,23DMB}$	300	150
$k_{LDF,nC6}/k_{LDF,22DMB}$	300	300

* $k_{LDF} = 15D_{nC6}/r^2$, where D_{nC6} (m².s⁻¹) is the diffusivity constant and r (m) is the crystallite radius of adsorbent particles. Taken from the ref.¹³

* Values calculated at 433 K.

The numerical simulations show that the mathematical model reasonably predicts the concentration profiles of the multicomponent breakthrough curves in most cases. It should be noted that it was only possible to qualitatively represent the experimental data by introducing strong diffusional resistances for the branched isomers (Table 4.7). However, the dynamic model shows some difficulties in matching the measured data at the lowest temperature of

373 K, where the interactions occurring inside the material due to competitive adsorption for preferential sites are higher, making it difficult to match the breakthrough curves profiles and overshoots. Probably, to better represent these breakthroughs, a robust adsorption model is necessary, requiring a more detailed mass transfer mechanism and a refined thermodynamic model to account for the interactions between the adsorbed molecules. But it is important to consider that while using a more complex adsorption model can improve the description of the experimental data, this increased complexity will augment the required time for the simulations. So, a compromise between complexity and practicality must be found to have a tool that can be both accurate and fast. Nevertheless, as a whole, the numerical results show that the simple LDF model associated with the empirical Sips isotherm is reasonable to describe comprehensively the main features that govern the sorption phenomena of complex mixtures of pentane and hexane isomers in ZIF-8.

The simulations assuming equal and high diffusivities for all pentane and hexane isomers (Figure B.3) reveal a completely different scenario, proving that the sorption of branched paraffins in ZIF-8 is strongly diffusional limited.

All the model parameters used for the simulations of experimental single and multicomponent breakthrough curves are summarised in Tables B.1 – B.9 of *Appendix B*.

4.4 Conclusions

We present here the first systematic experimental study dealing with the sorption of pentane and hexane isomers in the MOF ZIF-8. Multicomponent equimolar breakthrough curves of all hexane isomers exhibited a complete separation of the linear nC6 from its branched counterparts, based on equilibrium, and partial separation of mono- and di-branched isomers, via kinetic mechanisms, through their different diffusional limitations. However, since 2MP and 3MP components also started their elution at the beginning of experiments, it was not feasible to obtain a fraction with pure di-branched hexanes 23DMB and 22DMB.

The screening studies based on septenary mixtures of all pentane and hexane isomers followed the same trend observed in the hexane breakthroughs. At 373 K, the linear alkanes nC5 and nC6 were separated from their branched paraffins, followed by the partial separation between mono- and di-branched alkanes, resulting in a 92 RON ideal productivity of $0.176 \text{ mol.dm}^{-3}$. When the temperature increases to 473 K, the separation by classes is affected,

with nC5 reaching saturation even before iC5, 2MP, and 3MP. In the breakthrough experiments addressing only the branched alkanes, the partial separation between mono- (2MP/3MP) from di-branched (23DMB/22DMB) hexanes is evidenced. In addition, it is shown that the HRON iC5 (92.3) elutes from the column closer to the LRON 2MP (73.4) and 3MP (74.5), which is undesirable given the octane upgrading of gasoline.

The effect of the gas residence time in the sorption behaviour of branched alkanes is also evaluated. Accordingly, the higher this parameter, the higher their adsorption and the associated 92 RON ideal productivity.

The experimental data collected were correlated by the Sips isotherm and fitted parameters used in the dynamic mathematical model. The breakthrough simulations highlighted that kinetic limitation effects lead to very different sorption dynamics of branched alkanes, in which it was only possible to comprehensively describe their behaviour by accounting for low diffusivities due to strong diffusional limitations. The values that best matched the experimental data are: $k_{LDF,nC6} = k_{LDF,nC5} = 0.0300 - 0.117 \text{ s}^{-1}$; $k_{LDF,nC6}/k_{LDF,iC5} = k_{LDF,nC6}/k_{LDF,2MP} = k_{LDF,nC6}/k_{LDF,3MP} = 100$, $k_{LDF,nC6}/k_{LDF,23DMB} = 150$, and $k_{LDF,nC6}/k_{LDF,22DMB} = 300$.

Another important conclusion from this study concerns the experimental method used to measure the adsorption equilibrium of pentane and hexane isomers in ZIF-8 since experimental data obtained under flow systems or batch equilibrium conditions can be completely different. Nevertheless, if experimental conditions are carefully set up in flow systems, especially temperature and gas residence time, ZIF-8 can completely separate the linear paraffins from its branched isomers and partially separate mono- and di-branched alkanes. Also, this work shows the importance of using mathematical modelling to analyse and interpret experimental data to design adsorption-based separation processes. Finally, it must be concluded that the sorption of pentane and hexane isomers in ZIF-8 is a complex phenomenon that can be a major drawback for the development of TIP processes.

4.5 References

- (1) Henrique, A.; Rodrigues, A. E.; Silva, J. A. C. Separation of Hexane Isomers in ZIF-8 by Fixed Bed Adsorption. *Ind. Eng. Chem. Res.* **2019**, *58*, 378–394.
- (2) Henrique, A.; Rodrigues, A. E.; Silva, J. A. C. Fixed Bed Dynamics of Single and Multicomponent Adsorption of Pentane and Hexane Isomers in ZIF-8. *Sep. Purif.*

- Technol.* **2020**, *238*, 116419.
- (3) Ferreira, A. F. P.; Mittelmeijer-Hazeleger, M. C.; Granato, M. A.; Martins, V. F. D.; Rodrigues, A. E.; Rothenberg, G. Sieving Di-Branched from Mono-Branched and Linear Alkanes Using ZIF-8: Experimental Proof and Theoretical Explanation. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8795–8804.
- (4) Zhang, K.; Lively, R. P.; Zhang, C.; Chance, R. R.; Koros, W. J.; Sholl, D. S.; Nair, S. Exploring the Framework Hydrophobicity and Flexibility of ZIF-8: From Biofuel Recovery to Hydrocarbon Separations. *J. Phys. Chem. Lett.* **2013**, *4*, 3618–3622.
- (5) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. Separation of C6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A. *Ind. Eng. Chem. Res.* **2012**, *51*, 4692–4702.
- (6) Mendes, P. A. P.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Single and Multicomponent Adsorption of Hexane Isomers in the Microporous ZIF-8. *Microporous Mesoporous Mater.* **2014**, *194*, 146–156.
- (7) Zhang, L.; Qian, G.; Liu, Z.; Cui, Q.; Wang, H.; Yao, H. Adsorption and Separation Properties of N-Pentane/Isopentane on ZIF-8. *Sep. Purif. Technol.* **2015**, *156*, 472–479.
- (8) Chen, L.; Yuan, S.; Qian, J. F.; Fan, W.; He, M. Y.; Chen, Q.; Zhang, Z. H. Effective Adsorption Separation of N-Hexane/2-Methylpentane in Facilely Synthesized Zeolitic Imidazolate Frameworks ZIF-8 and ZIF-69. *Ind. Eng. Chem. Res.* **2016**, *55*, 10751–10757.
- (9) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069.
- (10) Silva, J. A. C.; Rodrigues, A. E. Equilibrium and Kinetics of N-Hexane Sorption in Pellets of 5A Zeolite. *AIChE J.* **1997**, *43*, 2524–2534.
- (11) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers

in a Metal-Organic Framework with Triangular Channels. *Science*. **2013**, *340*, 960–964.

- (12) Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press, 1998; Vol. 2.
- (13) Glueckauf, E. Formula for Diffusion into Spheres and Their Application to Chromatography. *Trans. Faraday Soc.* **1995**, *51*, 1540–1551.

5 HEXANE ISOMERS SEPARATION IN AN ISORETICULAR SERIES OF ZR CARBOXYLATES MOFs

The content of this chapter is based on:¹

- (1) Henrique, A.; Maity, T.; Zhao, H.; Brântuas, P. F.; Rodrigues, A. E.; Nouar, F.; Ghoufi, A.; Maurin, G.; Silva, J. A. C.; Serre, C. Hexane Isomers Separation on an Isorecticular Series of Microporous Zr Carboxylate Metal Organic Frameworks. *J. Mater. Chem. A* **2020**, *8*, 17780–17789.

Henrique, A.; Rodrigues, A. E.; Silva, J. A. C. Adsorption Dynamics of Hexane Isomers in the Microporous Zr Carboxylate Metal-Organic Framework MIL-140B. To be submitted

A series of isostructural Zr carboxylate MOFs, MIL-140A, B, and C, exhibiting 1D microporous triangular shaped channels and based on different aromatic dicarboxylate linkers, were investigated regarding their ability to separate hexane isomers. Single and equimolar multicomponent experiments were performed covering the temperatures of 343, 373, and 423 K and total alkane pressure up to 50.0 kPa using MIL-140B form. The elution order is similar to the normal boiling point of the compounds $nC6 > 2MP > 3MP > 23DMB > 22DMB$. Noteworthy, this material enables a thermodynamic-based separation of the hexane isomers by classes of linear ($nC6$), mono-branched (2MP/3MP), and di-branched (23DMB/22DMB) isomers with a selectivity up to 10, and a 92 RON ideal productivity up to $0.801 \text{ mol.dm}^{-3}$ at 343 K, decreasing, however, as the temperature increases. The Sips isotherm conveniently fitted the adsorption equilibrium, being the simulated breakthrough curves suitably predicted by the dynamic mathematical model. From the fitting of the experimental breakthrough curves, equal k_{LDF} coefficients for all hexane isomers were found, ranging from 0.0750 to 0.105 s^{-1} . The impact of the pore size in the series of isostructural Zr carboxylate MOFs was finally assessed by comparing data in MIL-140A and MIL-140C for multicomponent experiments at 343 K. A significant decrease in selectivity (about 2) was observed in both cases, while the loadings decreased or increased for MIL-140A and MIL-140C, respectively, in regard to the MIL-140B form.

5.1 Introduction

The conceptual approach by which a MOF is designed and assembled is called reticular synthesis and is based upon the identification of how well-defined molecular building blocks (secondary building units – SBUs) are assembled together using organic linkers of various lengths and geometries to form a net, or reticulate.^{2,3} Consideration of the geometric and chemical attributes of the molecular building blocks and organic linkers leads to the prediction of the framework topology.⁴ Reticular synthesis has become a core principle in MOFs science, showing that organic linkers of different lengths, but with a common geometry, can be used to generate MOFs of related topologies (isomorphic solids), but with increased pore sizes and volumes, leading to isorecticular series.⁵⁻⁷

A prominent example of this systematic design is the isorecticular series of MIL-140 porous materials, constructed from zirconium oxide SBUs and aromatic dicarboxylate linkers, featuring a general formula $[\text{ZrO}(\text{O}_2\text{C}-\text{R}-\text{CO}_2)]$ with $\text{R} = \text{C}_6\text{H}_4$, C_{10}H_6 , C_{12}H_8 and $\text{C}_{12}\text{N}_2\text{H}_6\text{Cl}_2$ for MIL-140A, MIL-140B, MIL-140C, and MIL-140D, respectively.⁷ On these solids, each SBU of complex zirconium oxide chains is connected to six other chains through the dicarboxylate linkers, delimiting one-dimensional triangular channels in its structure, as can be seen in Figure 5.1. The resulting pore widths of these four solids are 0.32, 0.40, 0.57, and 0.63 nm, associated with BET surface area from 350 up to 1000 $\text{m}^2\cdot\text{g}^{-1}$, respectively, this evolution being consistent with the gradual increase of the length of the organic linkers from MIL-140A to MIL-140D. In addition, this class of porous materials shows a pronounced hydrophobic character, a high hydrothermal, and good mechanical stability, which paves the way for their industrial application in catalysis, gas adsorption, and gas separation processes.

Two computational studies have recently been reported on the adsorption of hexane isomers in this isorecticular MIL-140s, revealing that these materials are not expected to show attractive separation performances.^{8,9} However, these conclusions merit reconsideration since these calculations were performed using a rigid framework, a critical assumption when one deals with the adsorption of bulky molecules in small pore MOFs. This encouraged us to conduct an unprecedented experimental exploration of the adsorption of hexane isomers on the MIL-140s. Moreover, it was shown in literature from breakthrough experiments that structures featuring one-dimensional triangular channels ($\text{Fe}_2(\text{BDP})_3$) are appealing for separating the hexane isomers by classes.⁹ Since the average pore aperture of the MIL-140 series covers the range of kinetic diameter of hexane isomers 0.43 – 0.62 nm, the study of these series is of high interest.

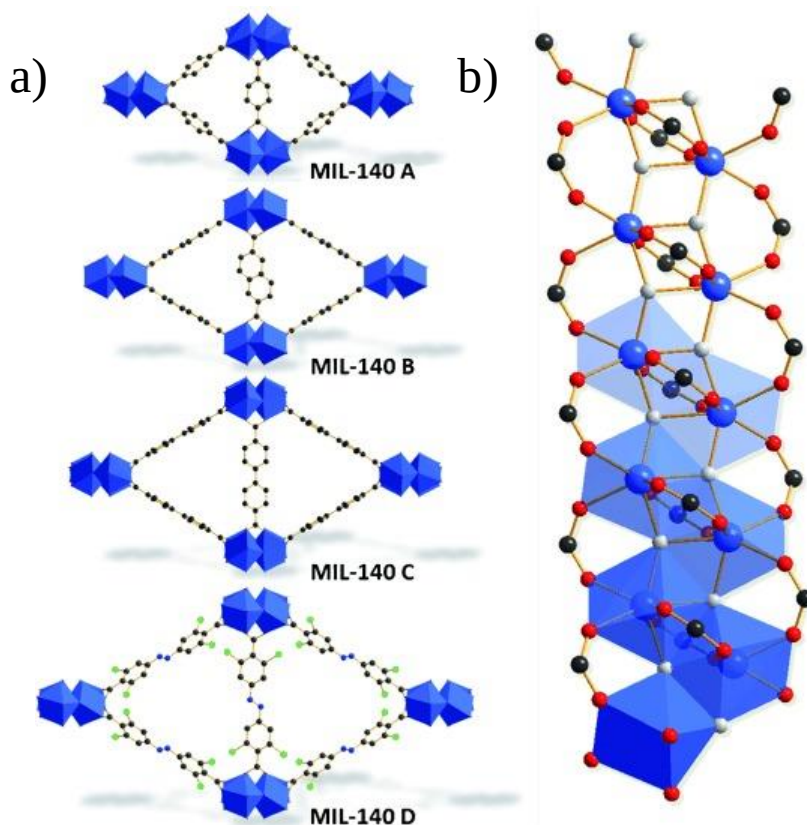


Figure 5.1 | Schematic view of MIL-140 series: a) view of the crystal structures along the c axis and b) view of the inorganic subunits. Zirconium atoms or polyhedra are blue, carbons atoms are black, and chlorine atoms are green. Oxygen atoms from the linker are red and oxo groups are grey. Adapted from the ref 7.

Therefore, the main objective of this chapter is to evaluate the potential of the microporous MIL-140 (A, B, and C) for separating hexane isomers. The first section of this chapter, Section 5.2, describes the methodology used to synthesize the MIL-140 materials. In addition, the structural and textural properties of the adsorbents are studied by a range of characterization techniques, including powder x-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and N_2 sorption isotherms. The adopted procedure used to transform the synthesized powdered material into small agglomerates for column packing is addressed in the sequence. In Section 5.3, the experimental and numerical results are shown. First, the adsorption behaviour of MIL-140B is explored *in-depth* by measuring single and multicomponent breakthrough curves, exploiting the effect of the temperature and alkane pressure. Then, the equilibrium data is modelled by the Sips isotherm and fitted parameters used in the dynamic mathematical model for the numerical simulations. Regarding MIL-140 A and C forms, screening tests addressing multicomponent mixtures of hexane isomers were performed, their selectivities being compared with the ones

obtained for MIL-140B. Finally, a summary of the key findings of the chapter is given in Section 5.4.

5.2 MIL-140s: Synthesis, Characterization, and Sampling

The synthesis and characterization of the MIL-140s was carried out at *Institut des Matériaux Poreux de Paris (IMAP)* of the *École Normale Supérieure de Paris (ENS)*.

5.2.1 Synthesis of MIL-140s

For the preparation of all MIL-140 solids, the following chemicals were used: zirconium chloride (ZrCl_4 , *Alfa Aesar*, 99.5+%), 1,4-benzenedicarboxylic acid (H_2BDC , *Sigma-Aldrich*, 98%), 2,6-naphthalenedicarboxylic acid (H_2NDC , *Alfa Aesar*, 98%), biphenyl-4,4'-dicarboxylic acid (H_2BPDC , *Acros Organics*, 98%) and acetic acid (*Merck*). All solvents N,N-dimethylformamide (DMF), ethanol, methanol, and acetone used for synthesis and purification are purchased from *Merck*. For all MIL-140s, the synthesis parameters were adapted from previously reported conditions:⁷

MIL-140A: 1.18 g (10 mmol) of ZrCl_4 and 1.68 g (10 mmol) of H_2BDC were mixed with 32 mL DMF solvent and put inside a 125 mL teflon autoclave. The autoclave was heated at 493 K for 12 h. After cooling to room temperature, the mixture was recovered by centrifugation, and the solid material was stirred with methanol overnight and dried in a vacuum oven.

MIL-140B: 0.7 g (3 mmol) of ZrCl_4 , 1.26 g (6 mmol) of H_2NDC , and 342 μL (6 mmol) of acetic acid was mixed with 15 mL DMF solvent and put inside a 125 mL teflon autoclave. The autoclave was heated at 493 K for 7 h. After cooling to room temperature, the mixture was recovered by centrifugation, and the solid material was stirred with methanol overnight and dried in a vacuum oven.

MIL-140C: 1.17 g (5 mmol) of ZrCl_4 , 2.42 g (10 mmol) of H_2BPDC , and 1430 μL (25 mmol) of acetic acid was mixed with 25 mL DMF solvent and put inside a 125 mL teflon autoclave. The autoclave was heated at 493 K for 12 h. After cooling to room temperature, the mixture was recovered by centrifugation, and the solid material was stirred with methanol overnight and dried in a vacuum oven.

5.2.2 Characterization of MIL-140s

All synthesized MOFs were fully characterized by PXRD, FTIR, TGA, and N₂ sorption isotherms. In addition, the MIL-140B sample was further analysed by scanning electron microscopy (SEM) for surface study.

5.2.2.1 PXRD of MIL-140s

The PXRD patterns were recorded with a diffractometer (*D8 ADVANCE, Bruker*) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Figure 5.2 shows a comparison of synthesized materials with their calculated powder pattern (extract from .cif), suggesting that the purity and quality of MIL-140s are very good and also match with reported data.⁷

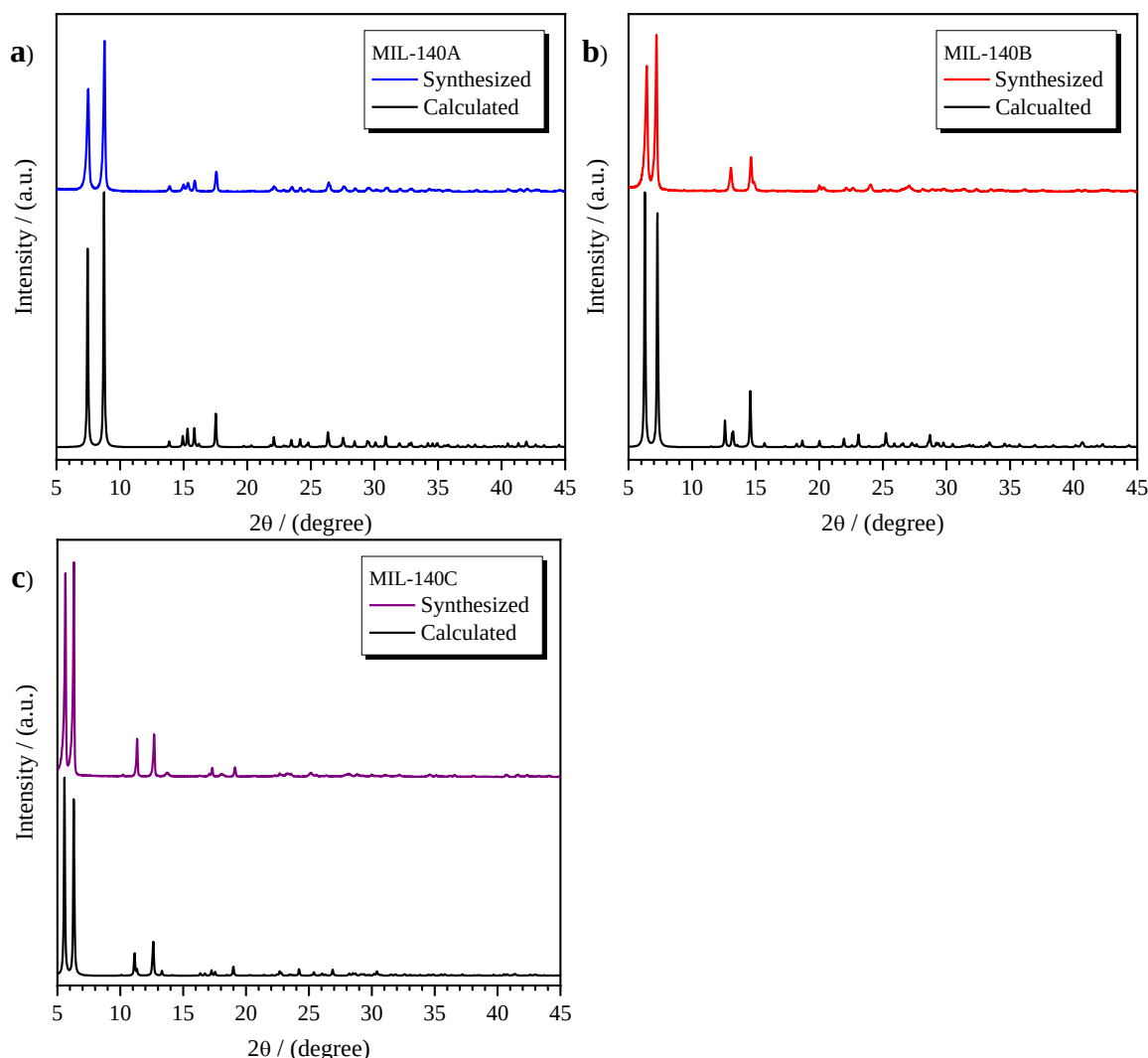


Figure 5.2 | PXRD of MIL-140s: a) MIL-140A, b) MIL-140B, and c) MIL-140C.

5.2.2.2 FTIR of MIL-140s

FTIR spectra were measured on a spectrometer (*Spectrum 100, Perkin-Elmer*) using the ATR technique. The spectrum of organic linkers H₂BDC, H₂NDC, and H₂BPDC and their corresponding materials MIL-140A, B, and C, respectively, reveals that there is no presence of unreacted solid linker in the MOF samples, as can be seen in Figure 5.3. Also, these results are well-matched with reported data.⁷ Characteristics bands are visible at: 1660, 1535, 1506, 1378, 1255, 1162, 1097, 1022, 883, 825, 743 and 660 cm⁻¹ for MIL-140A; 1606, 1540, 1490, 1409, 1361, 1205, 1143, 923 and 783 cm⁻¹ for MIL-140B; and 1573, 1507, 1400, 1180, 1109, 849, 763 and 680 cm⁻¹ for MIL-140C.

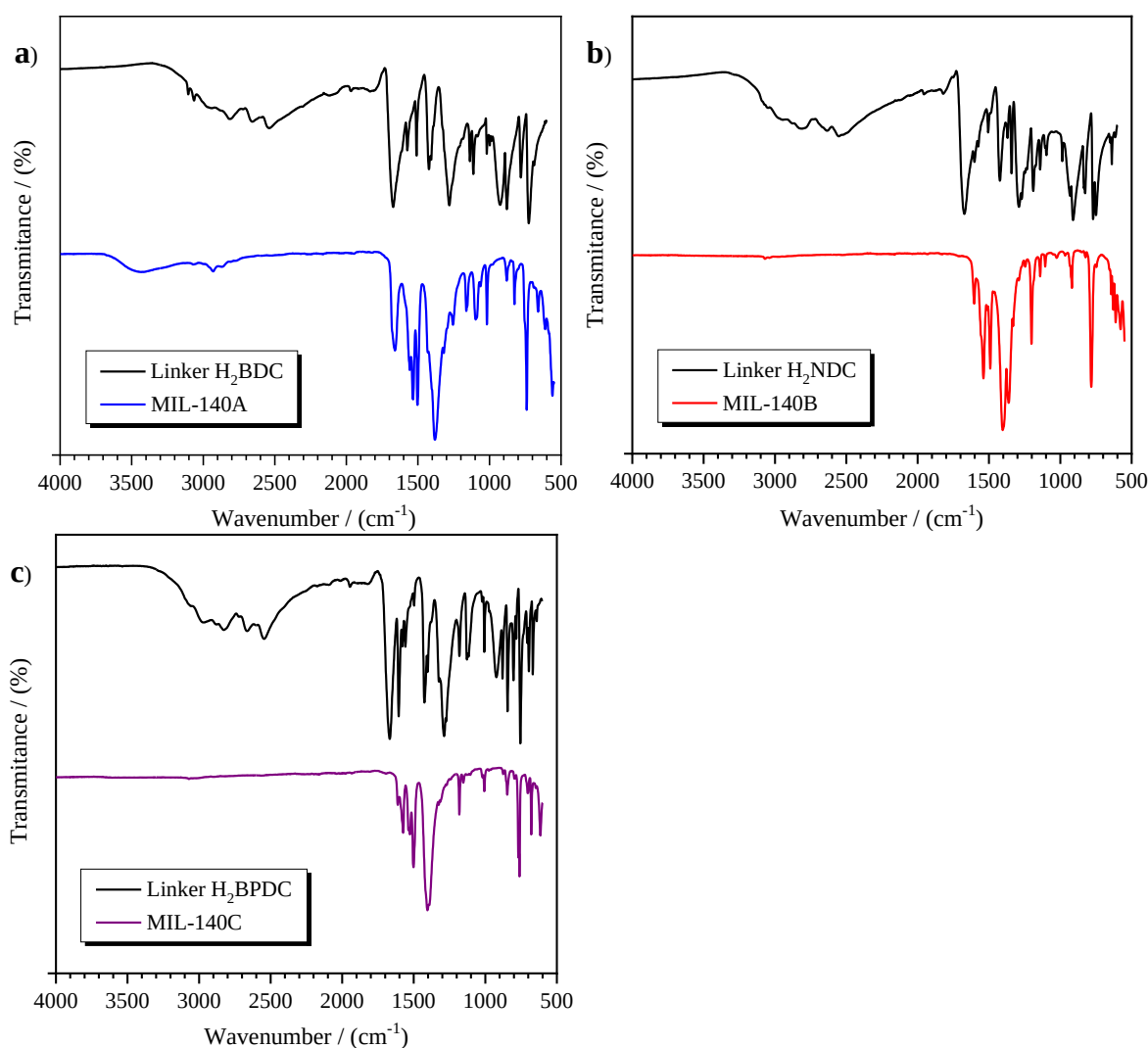


Figure 5.3 | FTIR spectra of MIL-140s: a) MIL-140A, b) MIL-140B, and c) MIL-140C.

5.2.2.3 TGA of MIL-140s

The TGA analysis, illustrated in Figure 5.4, was performed in a thermogravimetric analyser unit (*TGA2, Mettler Toledo*) under N_2 atmosphere (heating rate of $5\text{ K}\cdot\text{min}^{-1}$). The measurements confirm that MIL-140 A and B forms are thermally stable up to approximately 723 and 733 K, respectively. For the MIL-140C, the stability is slightly higher and goes up to 773 K. Above these temperatures, all materials show one big sharp weight loss due to the decomposition of the organic linker, in which the experimental and calculated values correspond to ≈ 51.3 and 54.5% for MIL-140A, ≈ 52.1 and 65.2% for MIL-140B, and ≈ 59.7 and 68.2% for MIL-140C, respectively.

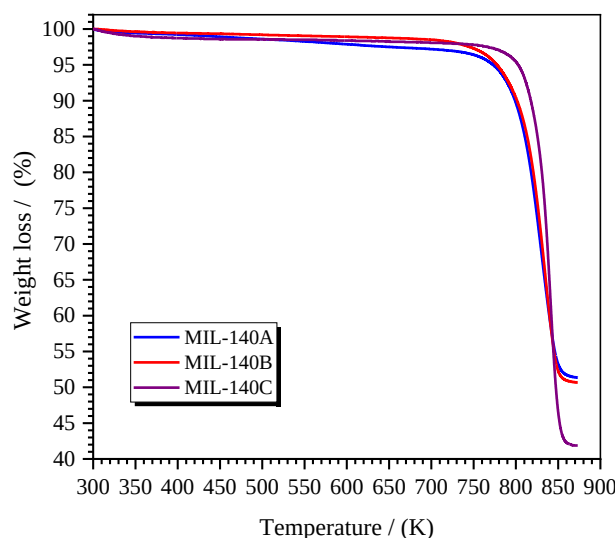


Figure 5.4 | TGA analysis of MIL-140s.

The ultrahigh stability of MIL-140s mainly comes from the strong coordinative interactions between $Zr(IV)$ ions of high charge density and the oxygen atoms of organic linkers.

5.2.2.4 N_2 Adsorption and Desorption Isotherms of MIL-140s

Gas sorption measurements were undertaken to understand the surface area of synthesized MIL-140 materials. N_2 adsorption and desorption isotherms were measured in a surface area and porosity analyser (*TriStar II Plus, Micromeritics*) at a temperature of 77 K and a pressure range of $0 - 10^5$ Pa. Prior to the experiments, the samples (≈ 50 mg) were evacuated at 393 K for 6 h under a vacuum atmosphere. The results are shown in Figure 5.5a, with the

isotherms being of type I according to the updated IUPAC classification, a typical characteristic of microporous materials.¹⁰ The N₂ adsorption progressively increases at the low-pressure region (p/p_0 between 10^{-5} to 10^{-2}) until reaching approximated loadings of 115, 120, and 200 cm³.g⁻¹ for MIL-140 A, B, and C forms, respectively, and then it practically remains constant until $p/p_0 = 1$.

The textural properties of MIL-140s, determined from the N₂ sorption measurements, such as specific surface areas, estimated using Brunauer-Emmett-Teller (S_{BET}) and Langmuir equations, both external surface area, microporous surface area, and micropore volume determined by the t -method, and the total pore volume calculated at $p/p_0 \approx 0.95$ are reported in Table 5.1.

To get knowledge on the porous nature of the materials, the Horvath-Kawazoe method (slit pore geometry) was used to represent the cumulative pore volume distribution as a function of the pore size, Figure 5.5b, showing a maximum pore volume of 0.16, 0.17, and 0.30 cm³.g⁻¹ for MIL-140 A, B, and C forms, respectively.

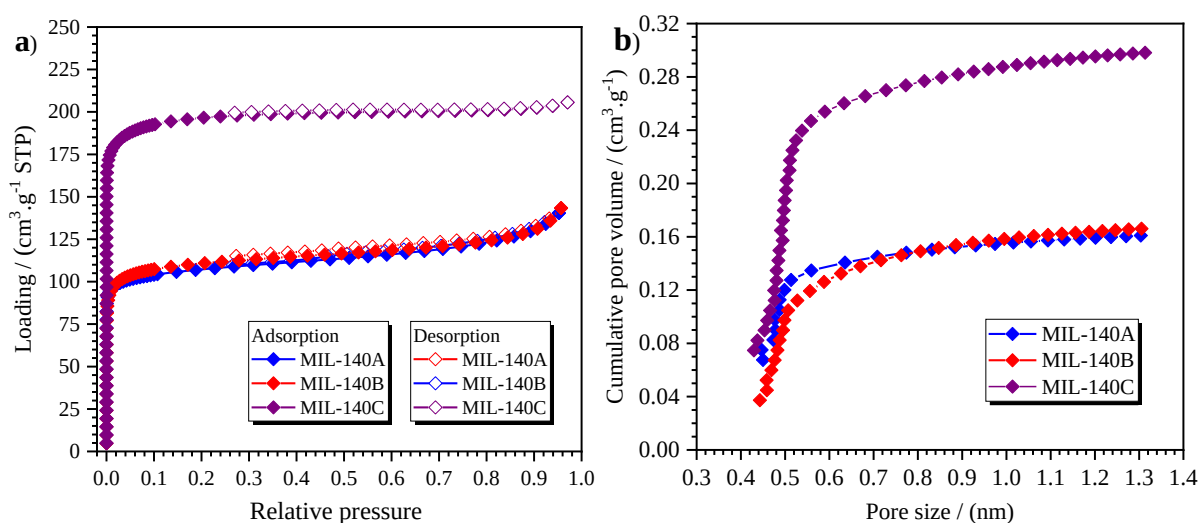


Figure 5.5 | N₂ sorption measurements at 77 K of MIL-140s: a) Adsorption and desorption isotherms **and b)** Cumulative pore volume distribution.

Table 5.1 | Textural properties of MIL-140s determined by N₂ sorption measurements.

		N ₂ sorption data		
		MIL-140A	MIL-140B	MIL-140C
S _{BET}	(m ² .g ⁻¹)	423	431	783
S _{Langmuir}	(m ² .g ⁻¹)	549	555	879
External surface area	(m ² .g ⁻¹)	70.4	72.5	78.2
Microporous surface area	(m ² .g ⁻¹)	353	359	704
Micropore volume	(cm ³ .g ⁻¹)	0.135	0.139	0.269
Total pore volume	(cm ³ .g ⁻¹)	0.216	0.218	0.316

5.2.2.5 SEM of MIL-140s

Scanning Electron Microscopic (SEM) image also signifies the formation of MIL-140B with purity, as can be seen in Figure 5.6. The flex-like shapes clearly prove the MIL-140B MOF material.¹¹

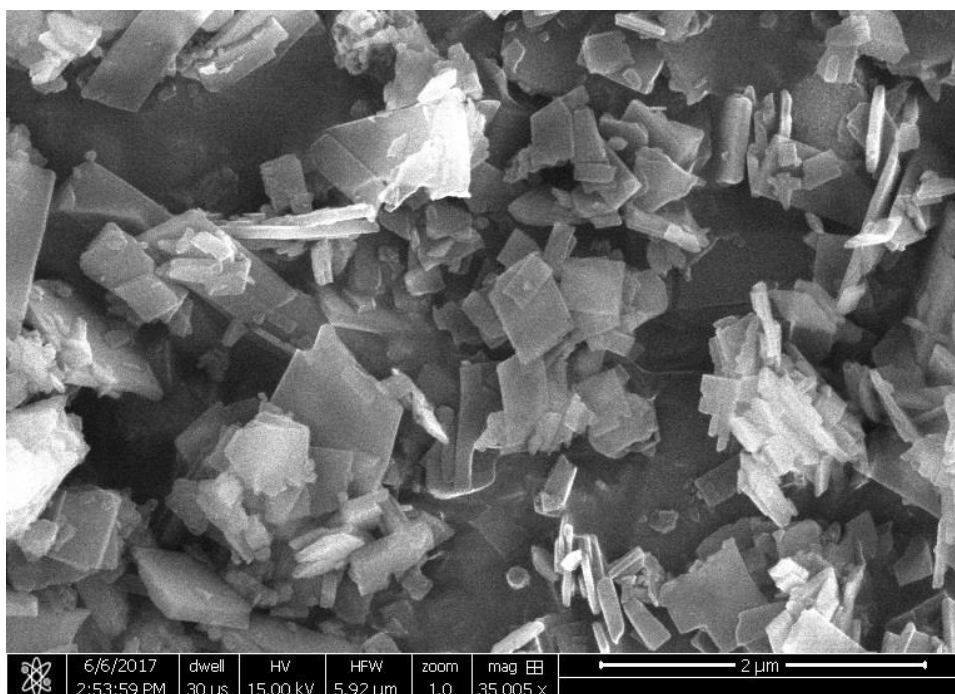


Figure 5.6 | SEM image of MIL-140B.

5.2.3 Sampling of MIL-140s

Prior to adsorption experiments, powdered MIL-140s were transformed into small agglomerates to minimize diffusion issues and avoid pressure drop, as depicted in Figure 5.7. First, the powder solids were compacted into tablets in a manual hydraulic press machine (*Atlas® 15T, Specac*); the pressure applied was 6.5 kg.mm^{-2} . Thereafter, the tablets were broken into small fragments and sieved to produce a known particle size distribution, which is around 2.5 mm.

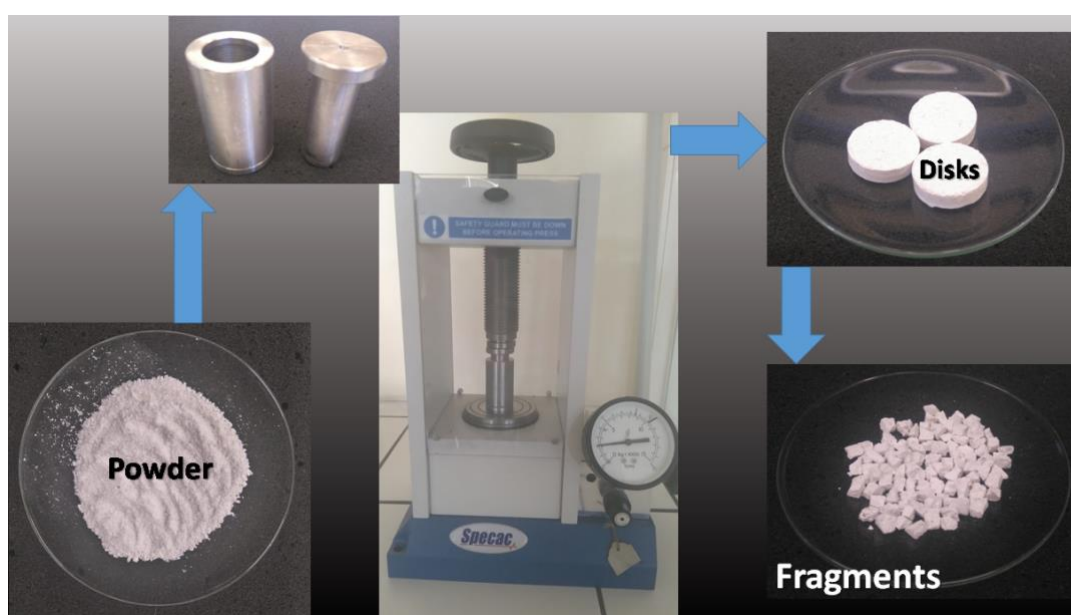


Figure 5.7 | Experimental procedure used for agglomeration of powdered MIL-140s.

5.3 Results and Discussion

5.3.1 Single Component Adsorption of Hexane Isomers in MIL-140B

Single component breakthrough curves of all hexane isomers in a fixed bed of MIL-140B were measured at three different temperatures, 343, 373, and 423 K, and with alkane partial pressure up to 50.0 kPa. Helium was used to set up a total pressure in the column of 101.3 kPa. Complete information on the experimental fixed bed runs performed, including the flow rates of alkane and He and also the equilibrium loadings, are detailed in Table 5.2. One can observe that the adsorption equilibrium hierarchy of hexane isomers in MIL-140B always fit the following trend: $n\text{C}_6 > 2\text{MP} > 3\text{MP} > 23\text{DMB} > 22\text{DMB}$, being similar to the normal

boiling point order of the components. Moreover, for all components, the equilibrium loadings increase as the alkane partial pressure increase (at a constant temperature) and decrease as the temperature increase (at a constant alkane partial pressure), therefore being thermodynamically consistent. An overall analysis showing the effect of these two working conditions in the single component breakthrough curves is given in Figures C.1 - C.3 of *Appendix C*.

Table 5.2 | Experimental conditions for measuring single component breakthrough curves of hexane isomers in MIL-140B and results.

Run	Temp. (K)	Alkane partial pressure (kPa)	Alkane flow rate ($\mu\text{mol}.\text{min}^{-1}$)	He flow rate ($\text{mL}.\text{min}^{-1}$)	q_i ($\text{mol}.\text{kg}^{-1}$)				
					22DMB	23DMB	3MP	2MP	nC6
<i>Single component: hexane isomers</i>									
1_2	343	5.00	11.6	5.00	0.0617	0.0792	0.199	0.229	0.418
1_3	343	10.0	24.5	5.00	0.0934	0.114	0.287	0.329	0.491
1_4	343	25.0	40.5	2.76	0.155	0.196	0.411	0.468	0.617
1_5	343	37.0	59.9	2.32	0.200	0.249	0.471	0.499	0.637
1_6	343	50.0	81.0	1.84	0.237	0.298	0.509	0.574	0.664
2_2	373	5.00	11.6	5.00	0.0398	0.0508	0.0900	0.114	0.216
2_3	373	10.0	24.5	5.00	0.0572	0.0731	0.134	0.176	0.330
2_4	373	25.0	40.5	2.76	0.0943	0.122	0.261	0.267	0.411
2_5	373	37.0	59.9	2.32	0.122	0.155	0.275	0.331	0.447
2_6	373	50.0	81.0	1.84	0.153	0.206	0.323	0.404	0.515
3_2	423	5.00	11.6	5.00	0.0183	0.0272	0.0481	0.0505	0.107
3_3	423	10.0	24.5	5.00	0.0362	0.0439	0.0651	0.0885	0.137
3_4	423	25.0	40.5	2.76	0.0571	0.0681	0.110	0.109	0.199
3_5	423	37.0	59.9	2.32	0.0751	0.0897	0.138	0.146	0.232
3_6	423	50.0	81.0	1.84	0.0917	0.110	0.161	0.178	0.256

The mass of MIL-140B used in the experiments was 630 mg, packed in column 1 (see Chapter 3);

The flow rates are expressed at STP conditions.

The corresponding adsorption equilibrium isotherms obtained from these experiments are shown in Figure 5.8. Whatever the temperature studied, all isotherms are of type I according to IUPAC classification.¹⁰ Additionally, a clear tendency for separating the hexane isomers by classes of linear (nC6), mono-branched (2MP/3MP), and di-branched (23DMB/22DMB)

isomers is expected at 343 K, especially at low alkane partial pressures (also indicated in Figure C.1). Noteworthy, this experimental observation drastically deviates significantly with the conclusions drawn from the molecular simulations previously reported by Dubbeldam et al., stating the adsorption of only linear and mono-branched alkanes.⁸

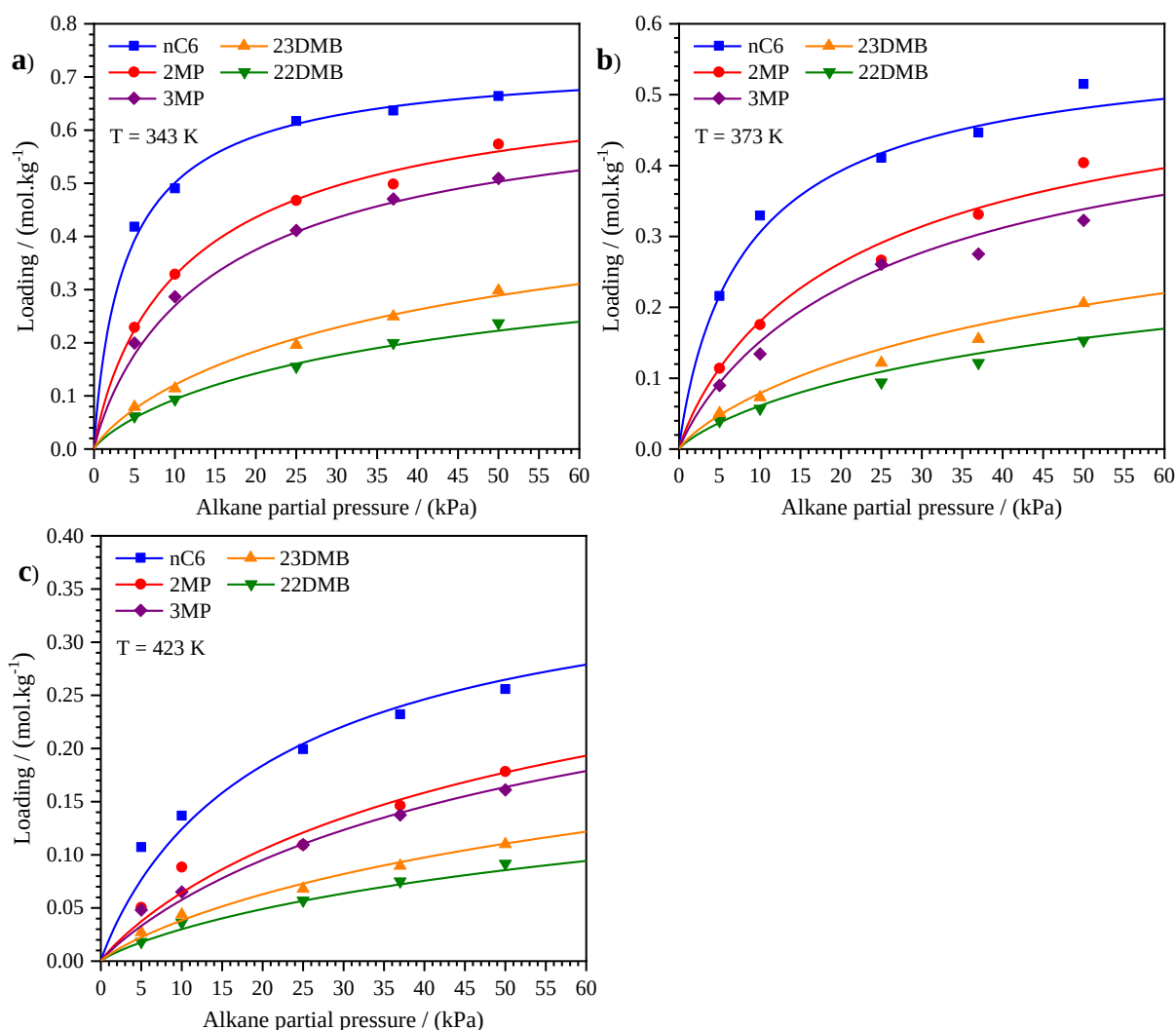


Figure 5.8 | Single component adsorption equilibrium isotherms of hexane isomers in MIL-140B: a) 343 K, b) 373 K, and c) 423 K. The continuous lines represent the Sips model predictions.

CBMC simulations performed in cooperation with *Institut Charles Gerhardt Montpellier (IGCM)* of the *Universite de Montpellier* were further considered to gain insight into the adsorption of all hexane isomers in MIL-140B. Results demonstrated that the simulations assuming a rigid model for the host framework significantly overestimated the corresponding experimental data in the whole pressure range, meaning that this consideration can hardly be applied to study the adsorption of bulky molecules in microporous MOFs like MIL-140B. Indeed, simulations accounting for a guest-induced reorientation of the linker

revealed that a relatively small tilting below 10° allows the reproduction of the experimental adsorption isotherms for all isomers. Regarding the preferential sittings of each isomer in the most representative tilted configurations, it was observed that the loading for nC6, 2MP and 3MP corresponds to 1 molecule per unit cell while 0.5 molecules per unit cell are considered for 22DMB and 23DMB. The molecules are arranged in such a way to interact with the organic linkers preferentially via their $-\text{CH}_3$ united atoms. Complete information about the molecular simulation procedures and detailed analysis of obtained results can be found on the published version.¹

5.3.2 Multicomponent Adsorption of Hexane Isomers in MIL-140B

To gain further insight on the adsorption of hexane isomers in MIL-140B, multicomponent breakthrough curves were measured with an equimolar quinary mixture of all five hexane isomers (nC6/2MP/3MP/23DMB/22DMB). The experiments were performed in the same range of temperature and alkane pressure covered in single components experiments. Table 5.3 summarizes the experimental conditions applied, the component loadings, the 92 RON ideal productivities, and the selectivities for each run performed. The mixture loading follows the same thermodynamic consistency observed in single component experiments.

Figures 5.9, 5.10, and 5.11 show the breakthrough curves for the temperatures of 343, 373, and 423 K, respectively. In each figure, the effect of total alkane pressure is shown: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The real-time RON of the product mixture leaving the column is also illustrated. The results indicate that the sorption hierarchy of hexane isomers in MIL-140B is always $\text{nC6} > 2\text{MP} > 3\text{MP} > 23\text{DMB} > 22\text{DMB}$, consistent with single component experiments. Moreover, at the lowest temperature 343 K (Figure 5.9), one can equally observe the ability of the material to fractionate the hexane isomers by the degree of branching, e.g., linear (nC6) > mono-branched (2MP, 3MP) > di-branched (23DMB, 22DMB) isomers, which is of major importance to obtain high RON values. Also, the RON values go up to 99 when only the di-branched hexanes 22DMB and 23DMB left the column separated from the other isomers. However, this sequence is strongly affected with increasing temperature, where at 423 K (Figure 5.11), the separation of branched isomers practically disappears, reducing the average RON values. At the highest temperature, a higher magnitude and faster rotation of the organic linkers are expected to be at the origin of the less-selective behaviour of MIL-140B.

The 92 RON ideal productivities (Eq. 3.4, *Chapter 3*) calculated using the framework density of MIL-140B, which is 1.55 g.cm^{-3} ,⁷ decreases with temperature and increases with total alkane pressure. At 343 K, where a separation by classes is seen, the values obtained at 25 kPa ($0.605 \text{ mol.dm}^{-3}$) and 50 kPa ($0.801 \text{ mol.dm}^{-3}$) are higher than the ones predicted by CBMC by Herm et al. for the benchmark MOF $\text{Fe}_2(\text{BDP})_3$ (0.54 mol.dm^{-3}).⁹ However, the value reported for this MOF was obtained at 433 K and 100 kPa of total alkane pressure, and at similar conditions, our data is significantly lower ($0.0933 \text{ mol.dm}^{-3}$, run 6_9).

In addition, in the breakthrough curves, we observe overshoots in concentration, where the least adsorbed components in the following order $22\text{DMB} < 23\text{DMB} < 3\text{MP} < 2\text{MP} < \text{nC6}$ are then desorbed by the more strongly adsorbed ones by an adsorption equilibrium competition displacement process. Since the least adsorbed components (moving faster in the column) are pushed off the adsorbent by the more strongly adsorbed ones (moving slower in the column), their concentration rises above the feed in a sequential manner. In the case of the di-branched isomers 22DMB and 23DMB, the rise in concentration can be 50% above that on the feed (Figure 5.9). This phenomenon puts in evidence the strong competition for sorption between di-branched, mono-branched, and linear paraffins, which is of major advantage for separating the hexane isomers in LRON and HRON fractions. As the temperature increases, these overshoots in concentration become smaller, as is the case observed at the temperature of 423 K (Figure 5.11) since the adsorption mixture loading is smaller.

Table 5.3 | Experimental conditions for measuring breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140s and results.

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol}.\text{min}^{-1}$)	He flow rate ($\text{mL}.\text{min}^{-1}$)	q_i ($\text{mol}.\text{kg}^{-1}$)					q_{mix} ($\text{mol}.\text{kg}^{-1}$)	P_s RON 92* ($\text{mol}.\text{dm}^{-3}$)	S_s
					22DMB	23DMB	3MP	2MP	nC6			
MIL-140B												
6_1	343	10.0	16.2	3.31	0.0163	0.0204	0.0515	0.0704	0.183	0.342	0.423	8.30
6_2	343	25.0	40.5	2.76	0.0180	0.0249	0.0704	0.0960	0.254	0.463	0.605	9.79
6_3	343	50.0	81.0	1.84	0.0221	0.0290	0.0874	0.115	0.309	0.562	0.801	10.0
6_4	373	10.0	16.2	3.31	0.0126	0.0180	0.0313	0.0394	0.0951	0.196	0.174	5.42
6_5	373	25.0	40.5	2.76	0.0165	0.0212	0.0476	0.0602	0.160	0.305	0.307	7.09
6_6	373	50.0	81.0	1.84	0.0191	0.0263	0.0578	0.0734	0.194	0.371	0.408	7.17
6_7	423	10.0	16.2	3.31	0.0102	0.0120	0.0155	0.0161	0.0313	0.0850	0.0293	2.83
6_8	423	25.0	40.5	2.76	0.0143	0.0169	0.0271	0.0287	0.0523	0.139	0.0876	3.46
6_9	423	50.0	81.0	1.84	0.0176	0.0218	0.0313	0.0342	0.0710	0.176	0.0933	3.47
MIL-140A												
7_1	343	10.0	16.2	3.31	0.0383	0.0538	0.0656	0.0625	0.0826	0.303	0.103	2.29
7_2	343	25.0	40.5	2.76	0.0461	0.0654	0.0802	0.0754	0.102	0.369	0.126	2.31
7_3	343	50.0	81.0	1.84	0.0730	0.0724	0.0921	0.0851	0.126	0.448	-	2.08
MIL-140C												
8_1	343	10.0	16.2	3.31	0.228	0.280	0.359	0.296	0.359	1.52	0.0875	2.00
8_2	343	25.0	40.5	2.76	0.233	0.284	0.361	0.297	0.318	1.49	-	1.89
8_3	373	50.0	81.0	1.84	0.247	0.284	0.376	0.304	0.332	1.54	-	1.91

The mass of MIL-140A, B, and C used in the experiments was 650, 614, and 536 mg, respectively, packed in column 1 (see Chapter 3);

The flow rates are expressed at STP conditions;

* Since the MIL-140s are in the powdered form, the volumetric productivities were calculated using their respective framework density.

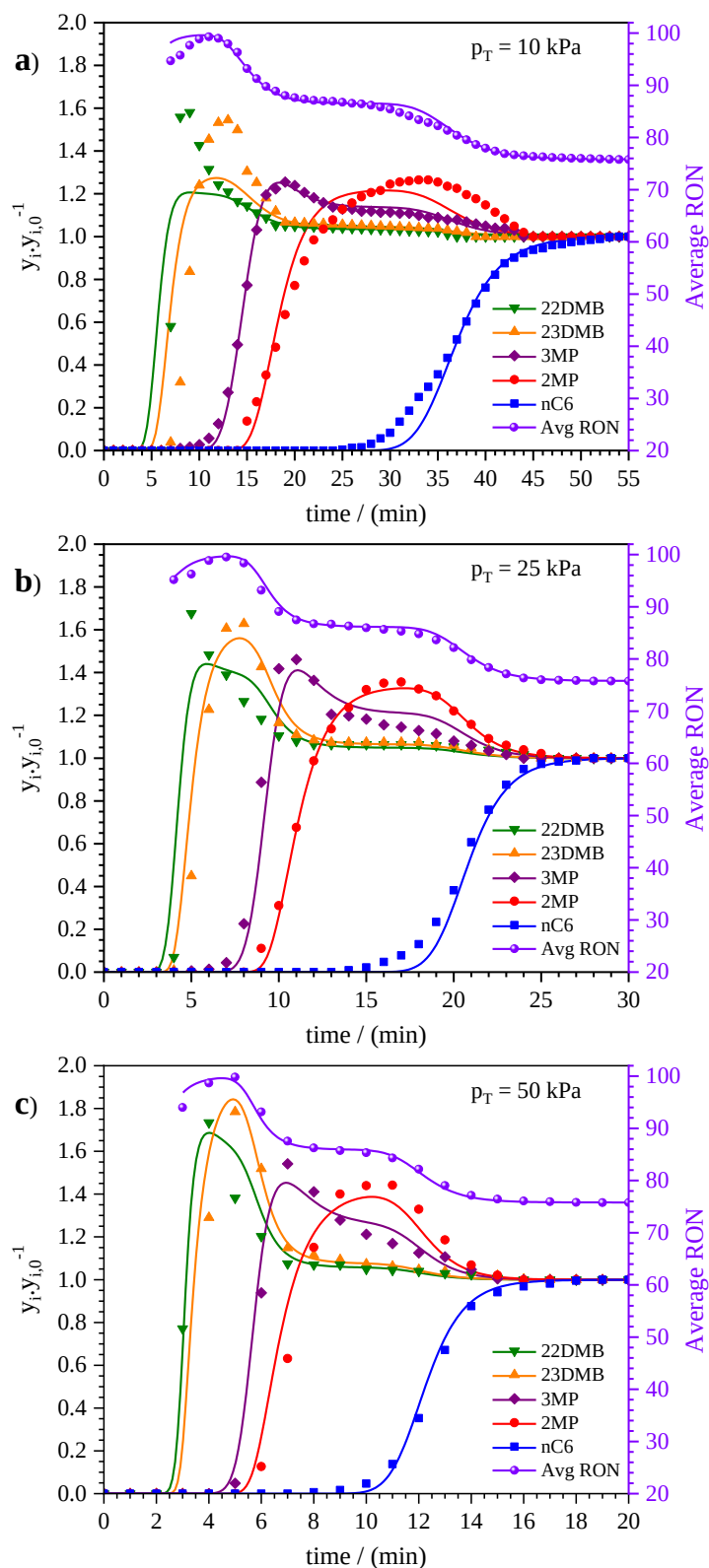


Figure 5.9 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 343 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

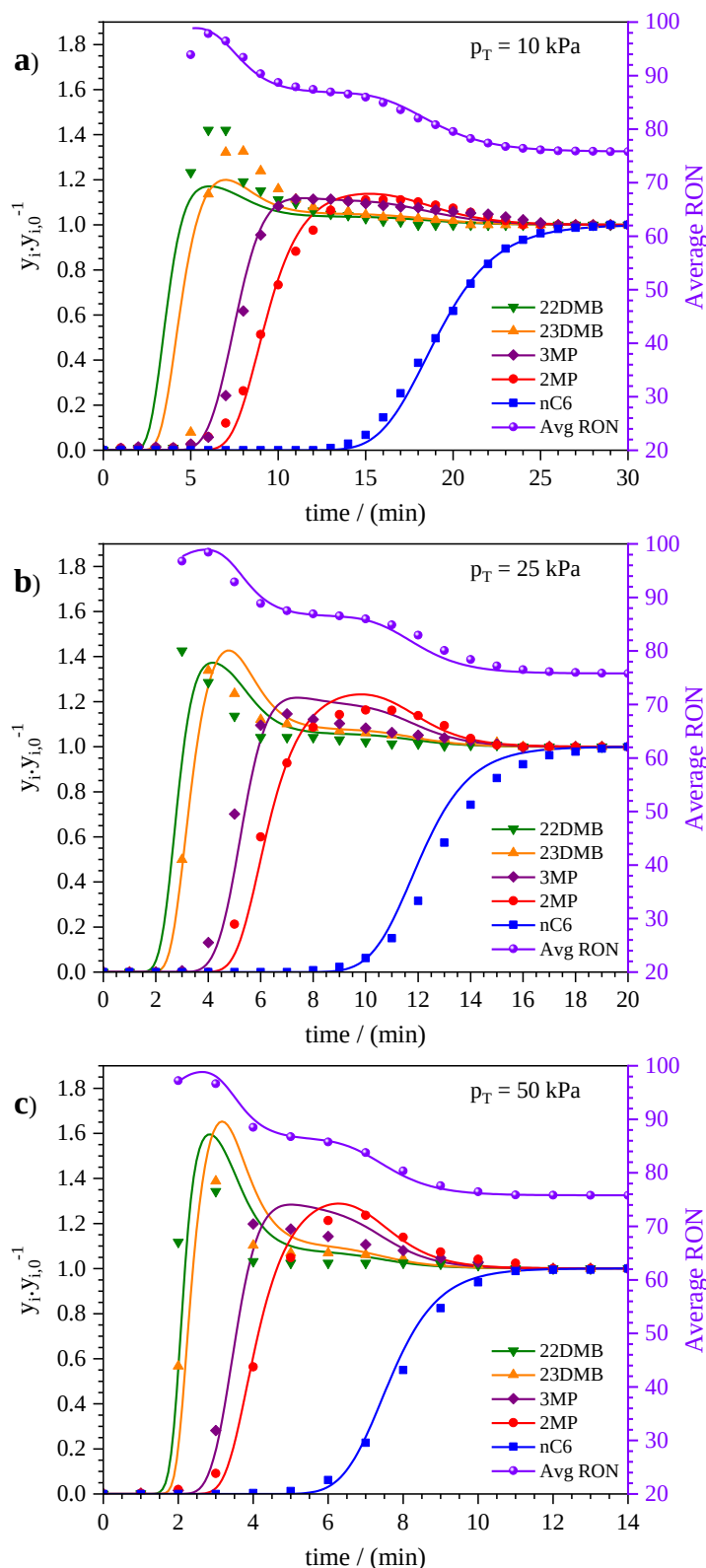


Figure 5.10 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 373 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

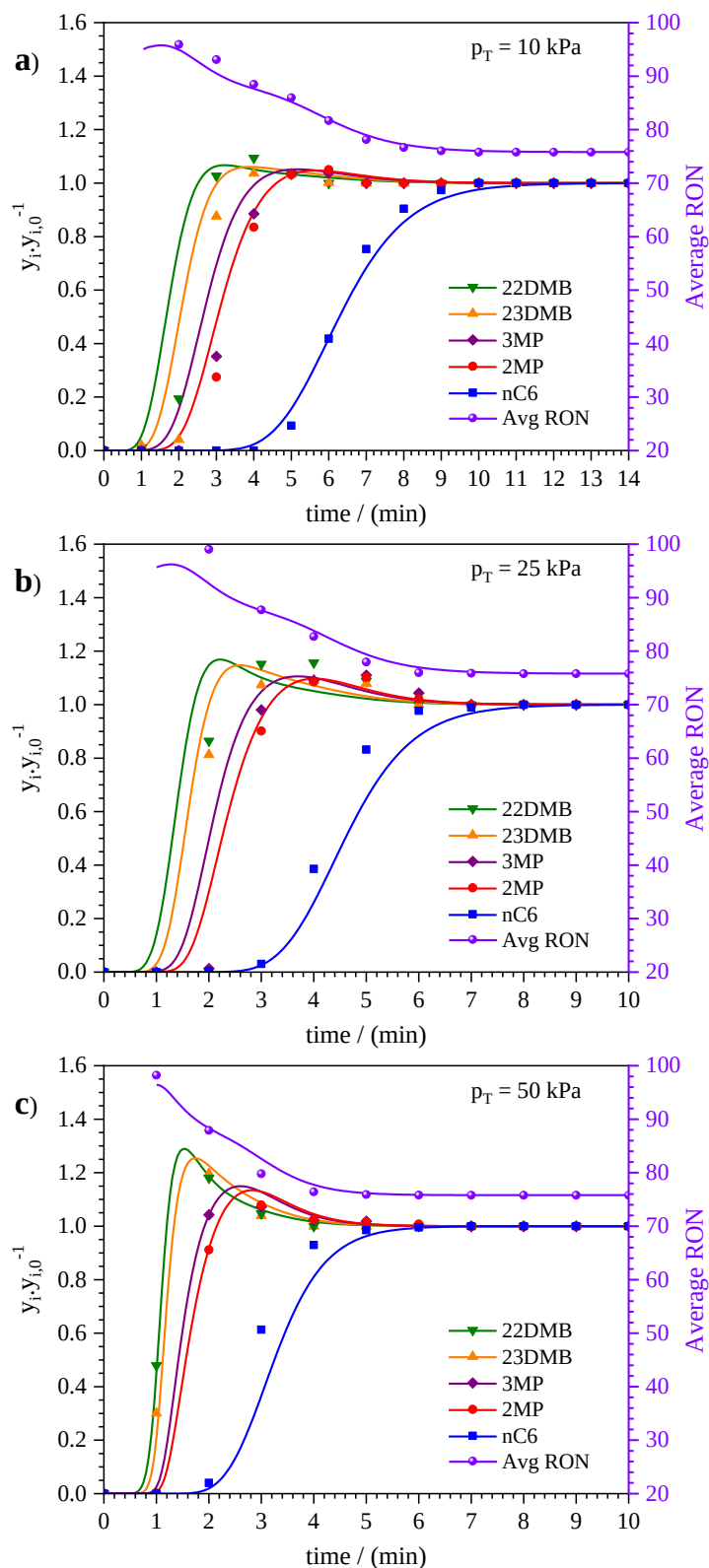


Figure 5.11 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 423 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

The selectivities from multicomponent experiments, measured by the ratio of the loadings between linear + mono-branched paraffins over the di-branched ones (Eq. 3.5, *Chapter 3*), are displayed as a function of total alkane pressure in Figure 5.12. They range from around 10 at 343 K to 3 at 423 K and maintain practically constant in the range of total alkane pressure studied.

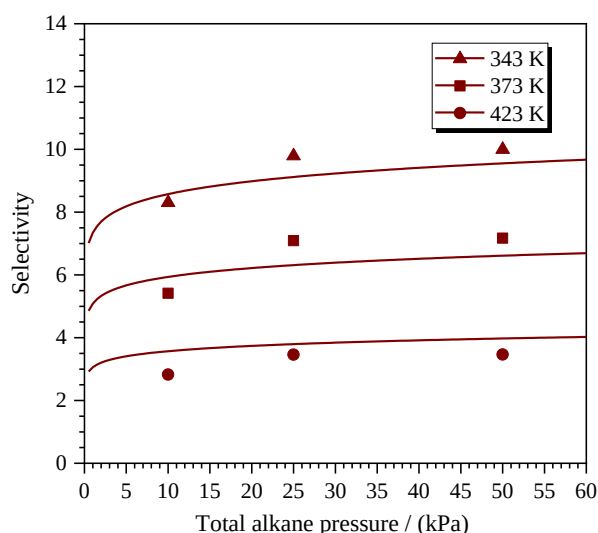


Figure 5.12 | Sorption selectivities of hexane isomers in MIL-140B. The continuous lines represent the Sips model predictions.

Figure 5.13 shows the quinary adsorption equilibrium isotherms of hexane isomers in MIL-140B. Again, the isotherms are of type I according to the IUPAC classification.¹⁰ One also can note that, globally, the amount adsorbed of linear nC6 is around twice higher than that of branched isomers, mostly due to steric hindrance of the bulkier isomers that prevent from a larger adsorption within the very narrow pores of MIL-140B. It is also observed that the loadings of hexane isomers are separated based on their class, (nC6) > mono-branched (2MP/3MP) > di-branched (23DMB/22DMB), especially at 343 K.

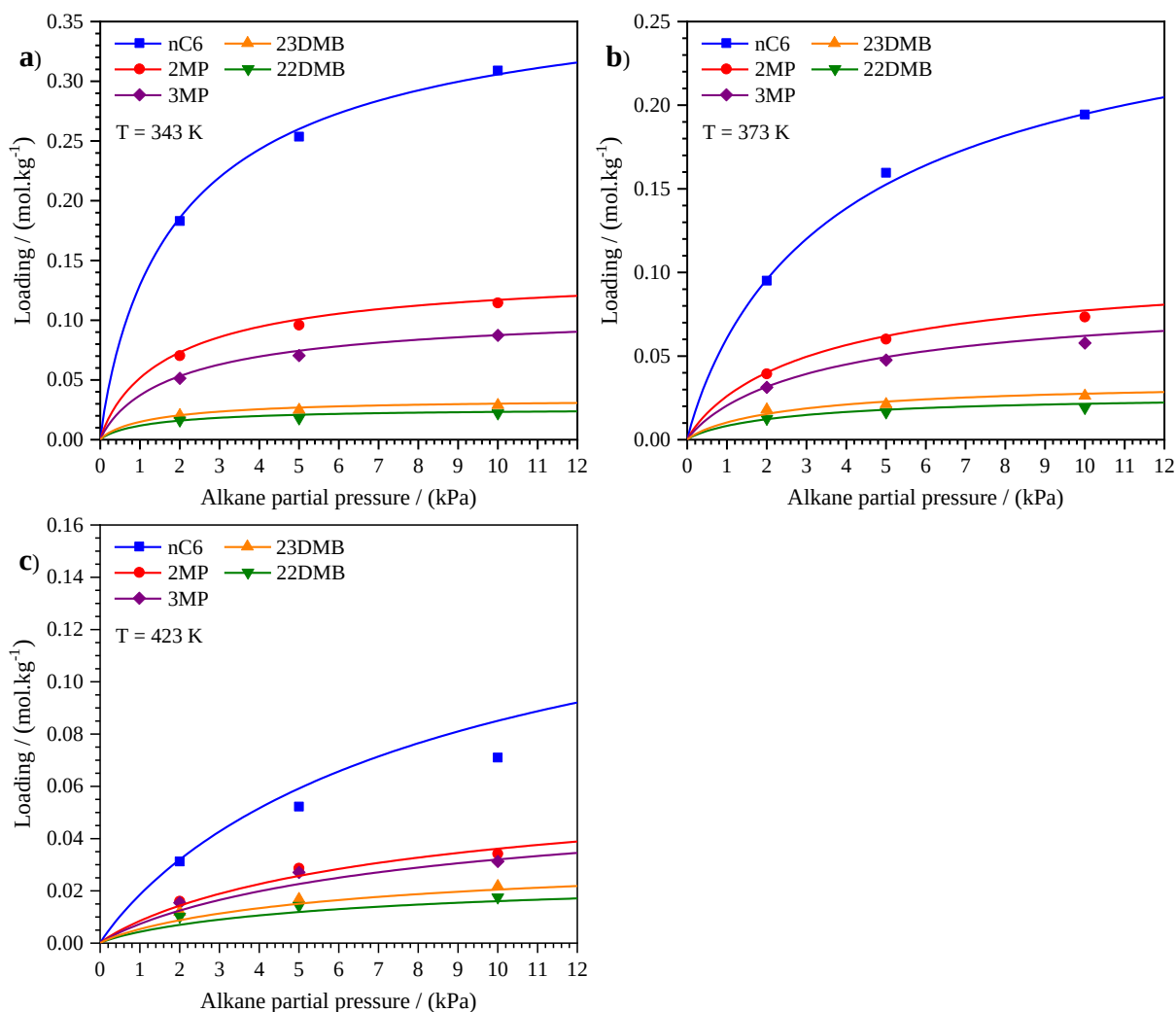


Figure 5.13 | Quinary adsorption equilibrium isotherms of hexane isomers in MIL-140B: a) 373 K, b) 423 K, and c) 473 K. The continuous lines represent the Sips model predictions.

5.3.3 Modelling Adsorption Equilibrium Isotherms

The fitting results for the single and multicomponent quinary isotherms of hexane isomers in MIL-140B have already been shown in Figures 5.8 and 5.13 by the continuous lines, respectively. As exhibited, a proper description of their adsorption behaviour was obtained. For the fitting procedure, the loadings obtained from the single (Table 4.3) and multicomponent (Table 4.4) breakthrough experiments were correlated with the Sips isotherm model described in *Chapter 3*. One can also note that the selectivities predicted by the model in Figure 5.12 show similar behaviour to the experimental ones.

The obtained model parameters are reported in Table 5.4. As it can be seen, q_{sat} , b , and ΔH (magnitude) are compatible with the sorption hierarchy order observed in the breakthrough experiments: $nC6 > 2MP > 3MP > 23DMB > 22DMB$. At 343K, the ratio between the affinity

constants of linear over mono-branched (nC6/2MP) and mono- over di-branched (3MP/23DMB) isomers is around 3, reflecting their separation by classes at a given temperature. Considering the system heterogeneity, the characteristic parameter n is close to the unit for all components (with the highest value being 1.23 for the 22DMB at 343 K), showing that the heterogeneity is low. In addition, they slightly decrease with temperature, suggesting that the system is apparently less heterogeneous as temperature increases. To simplify the fitting procedure, it was assumed that the effect of the temperature over the parameters q_{sat} and n are equal for all isomers.

Table 5.4 | Sips isotherm parameters for the sorption of hexane isomers in MIL-140B and average deviation between model predictions and experimental data.

Sips parameters		Hexane isomers				
		nC6	2MP	3MP	23DMB	22DMB
$-\Delta H_i$	(kJ.mol ⁻¹)	25.6	22.9	19.7	9.08	9.04
δ	(-)	2.73	2.73	2.73	2.73	2.73
$n_{0,i}^*$	(-)	1.13	1.15	1.13	1.22	1.23
α	(-)	0.150	0.150	0.150	0.150	0.150
<i>Temperature: 343 K</i>						
$q_{sat1,i}$	(mol.kg ⁻¹)	0.741	0.730	0.691	0.584	0.456
$b_{1,i}$	(kPa ⁻¹)	0.229	0.0785	0.0605	0.0195	0.0189
$n_{1,i}$	(-)	1.13	1.15	1.13	1.22	1.23
<i>Temperature: 373 K</i>						
$q_{sat2,i}$	(mol.kg ⁻¹)	0.584	0.575	0.544	0.460	0.359
$b_{2,i}$	(kPa ⁻¹)	0.111	0.0411	0.0348	0.0151	0.0146
$n_{2,i}$	(-)	1.11	1.13	1.11	1.20	1.21
<i>Temperature: 423 K</i>						
$q_{sat3,i}$	(mol.kg ⁻¹)	0.392	0.386	0.365	0.309	0.241
$b_{3,i}$	(kPa ⁻¹)	0.0420	0.0172	0.0164	0.0107	0.0104
$n_{3,i}$	(-)	1.09	1.11	1.09	1.18	1.19
$\Sigma \bar{\Delta}q$		0.00842				

* The reference temperature used was $T_0 = 343$ K.

5.3.4 Numerical Simulations of Multicomponent Breakthrough Curves

The numerical simulations for the multicomponent breakthrough curves of hexane isomers in MIL-140B, using the dynamic mathematical model described in *Chapter 3*, have already been shown in Figures 5.9 - 5.11 by the continuous lines. The steepness of the breakthrough components associated with the overshoots in the concentration of branched isomers indicates that their separation essentially results from thermodynamic effects based on adsorption equilibrium competition and is not diffusion controlled. Thus, the simulations accounted for weak diffusional resistances (high diffusivities). The k_{LDF} coefficients (Eq. 3.22, *Chapter 3*) found to obtain the best fit of the experimental data range from 0.0750 s^{-1} (343 K) to 0.105 s^{-1} (423 K) for all hexane isomers. Their temperature dependence, which follows the Arrhenius form (Eq. 3.23, *Chapter 3*), gave rise to an ΔE_i of 5 kJ.mol^{-1} . In addition, the simulations revealed that the system is isothermal.

Globally, a good agreement between the numerical predictions and experimental observations is obtained, being the shape of the breakthrough curves, including the overshoot phenomena for branched isomers qualitatively described in most cases. The main deviations are found in predicting the high experimental overshoots of di-branched isomers 23DMB and 22DMB at the lowest partial pressure (10 kPa) at 343 and 373 K. Nevertheless, an overall perspective of these results shows that the extended Sips isotherm, coupled with the LDF-based mathematical model, is suitable for comprehensively analysing the sorption phenomena of hexane isomers in MIL-140B.

All the model parameters used for the simulations of experimental multicomponent breakthrough curves are reported in Tables C.1 – C.3 of *Appendix C*.

5.3.5 Impact of the Pore Size

Adsorption screening studies were further performed for MIL-140A and MIL-140C through multicomponent breakthrough curves with equimolar mixtures of hexane isomers at 343 K to probe the effect of the pore size over the separation of isomers, MIL-140A having the smallest pore size and MIL-140C the largest of the series. Experimental conditions and obtained component loadings, ideal productivities, and selectivities are summarised in Table 5.3, together with the results obtained in MIL-140B for comparison. Figures 5.14 and 5.15 report

the experimental breakthroughs for MIL140A and MIL-140C forms, respectively, at the total alkane pressures of a) 10 kPa, b) 25 kPa, and c) 50 kPa.

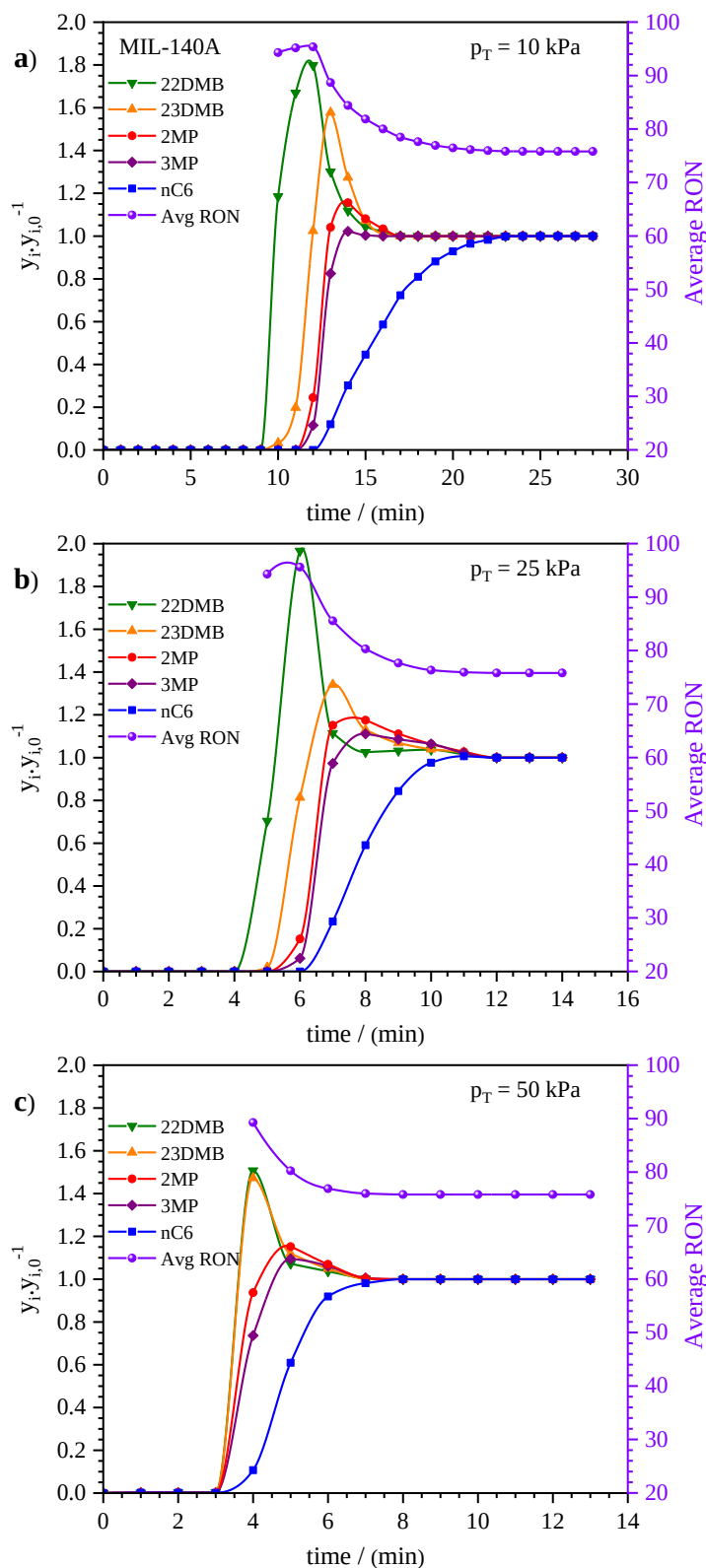


Figure 5.14 | Experimental breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140A at 343 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa.

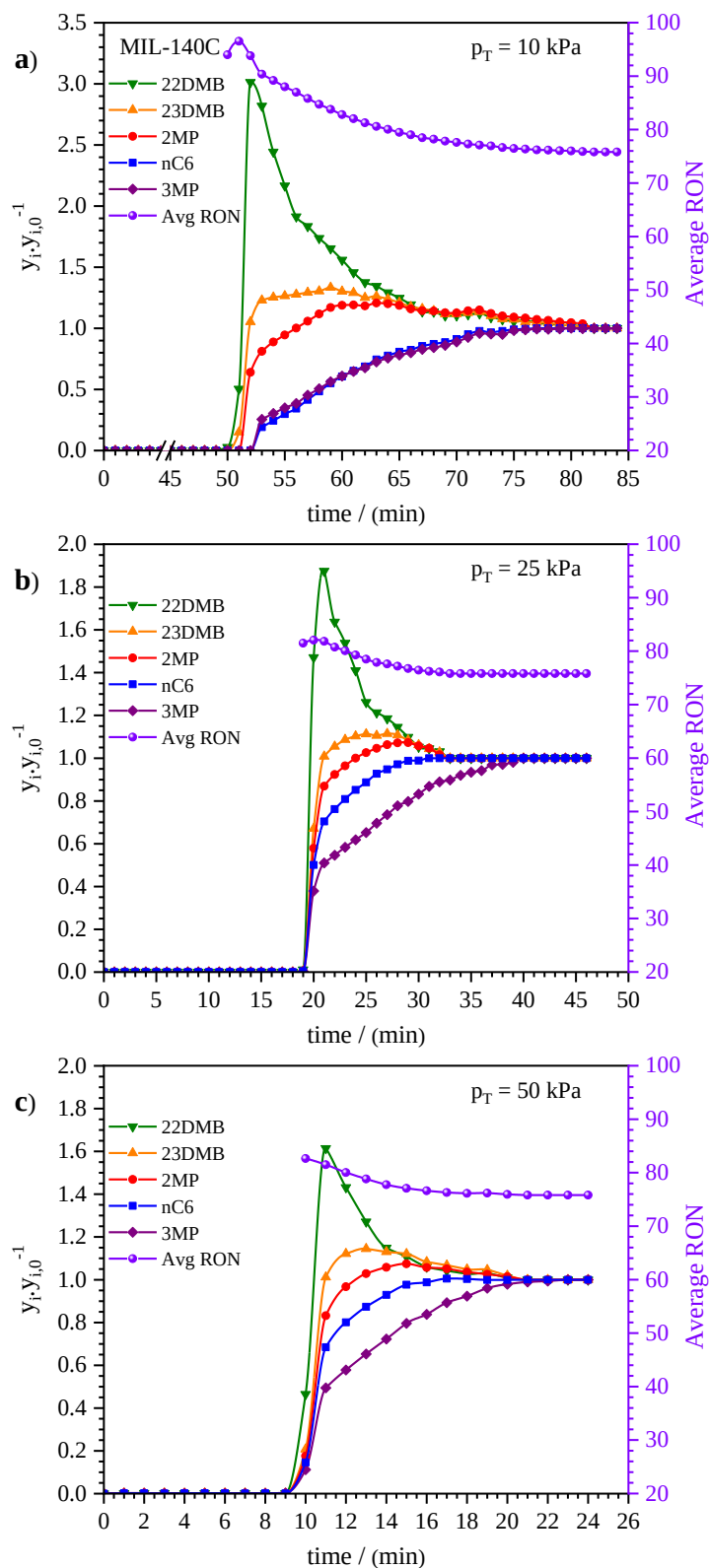


Figure 5.15 | Experimental breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140C at 343 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa.

It comes that MIL-140A and MIL-140C cannot separate the hexane isomers with the same degree of selectivity as those exhibited by MIL-140B, as depicted in Figure 5.16.

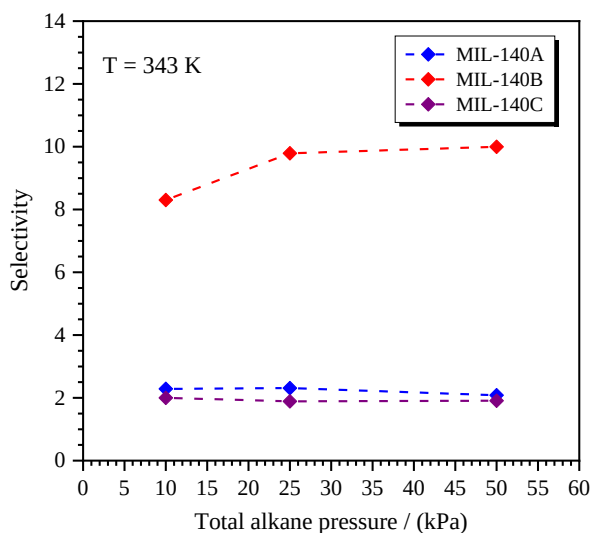


Figure 5.16 | Comparison between sorption selectivities of hexane isomers in MIL-140s at 343 K.

The selectivity values are much smaller in MIL-140A and MIL-140C (around 2) than MIL-140B (around 10). Furthermore, the experiments performed on MIL-140A (Figure 5.14) show a sorption hierarchy following the order of the normal boiling point of the compounds $nC6 > 3MP \geq 2MP > 23DMB \geq 22DMB$ with comparable mixture loadings, but without a pronounced separation by classes as observed in MIL-140B. It is to be noted that these experimental findings again contradict the previous simulations stating that none of the hexane isomers can be adsorbed in MIL-140A.^{8,9} The 92 RON ideal productivities, calculated with the framework density of MIL-140A, which is 1.74 g.cm^{-3} ,⁷ were found to be equal to 0.103 and $0.126 \text{ mol.dm}^{-3}$ at the total alkane pressure of 10 and 25 kPa , respectively. These values are substantially lower than the ones obtained at the same conditions in MIL-140 B form, which are 0.423 and $0.605 \text{ mol.dm}^{-3}$, respectively.

Regarding MIL-140C, a completely different picture is obtained. Figure 5.15 shows that all hexane isomers elute practically at the same time but with a different profile to saturation. This wavefront (containing all the compounds) that elutes from the column after a certain time is itself a separation wavefront, which is an uncommon behaviour. A change in the elution order of the compounds relative to their normal boiling point order is observed, where the mono-branched 3MP is the last component to saturate in the column. In other words, there is a shift between 3MP and nC6 in the elution order. Consequently, the sorption hierarchy is $3MP \geq nC6 > 2MP > 23DMB > 22DMB$ that drastically differs from the sequence predicted by the two

previous molecular simulation studies ($23\text{DMB} \approx 3\text{MP} \approx 2\text{MP} \approx \text{nC6} \approx 22\text{DMB}$).^{8,9} This suggests the critical role of the linker rotation in the sorption properties of MIL-140C, even if its pore size is significantly larger than the A- and B- analogues. The 92 RON ideal productivity (framework density of MIL-140C: 1.23 g.cm^{-3})⁷ was only possible to be measured at the total alkane pressure of 10 kPa, being equal to $0.0875 \text{ mol.dm}^{-3}$, which is the lowest value obtained between the three materials at the same working conditions. Finally, the loading of the hexane isomers in MIL-140C is much higher than the ones observed in MIL-140A and MIL-140B. Table 5.3 indicates a mixture loading around 1.5 mol.kg^{-1} in MIL-140C, which is more than twice higher than the loadings obtained for MIL-140A and MIL-140B. This trend is consistent with its much higher S_{BET} ($783 \text{ m}^2.\text{g}^{-1}$) and cumulative pore volume ($0.32 \text{ cm}^3.\text{g}^{-1}$) that facilitates the adsorption of all isomers, especially the di-branched ones.

5.4 Conclusions

We report here the first experimental study on the sorption of hexane isomers in the isorecticular series of Zr oxide dicarboxylate MOFs MIL-140s (A, B, and C). Single and multicomponent (equimolar) breakthrough curves demonstrated that MIL-140B could separate the hexane isomers by classes of linear (nC6), mono-branched (2MP, 3MP), and di-branched (23DMB, 22DMB) isomers at low temperature (343 K) together with a high selectivity up to 10, and a 92 RON ideal productivity up to $0.801 \text{ mol.dm}^{-3}$. At higher temperatures, the separation progressively disappears. The experimental data were fitted with the Sips isotherm and the obtained parameters used in the numerical simulations. With the use of equal k_{LDF} coefficients for all hexane isomers, an appropriate description of their competition behaviour observed in the multicomponent breakthrough curves was obtained.

Finally, the impact of the pore size and the nature of the organic spacer were assessed on MIL-140 A and MIL-140C. The smaller pores MIL-140A showed a hexane isomers sorption hierarchy according to the normal boiling point order of the compounds, while the larger pores MIL-140C exhibited a mixed sorption hierarchy with a very uncommon shift in the elution order between 3MP and nC6. In conclusion, concerning potential strategies for octane number enhancement (separation between di-branched isomers and the mono/linear ones), results obtained with MIL-140B are encouraging, especially at 343 K with a clear trend for separation by classes.

5.5 References

- (1) Henrique, A.; Maity, T.; Zhao, H.; Brântuas, P. F.; Rodrigues, A. E.; Nouar, F.; Ghoufi, A.; Maurin, G.; Silva, J. A. C.; Serre, C. Hexane Isomers Separation on an Isoreticular Series of Microporous Zr Carboxylate Metal Organic Frameworks. *J. Mater. Chem. A* **2020**, *8*, 17780–17789.
- (2) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705–714.
- (3) Rowsell, J. L. C.; Yaghi, O. M. Metal-Organic Frameworks: A New Class of Porous Materials. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.
- (4) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (5) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469–472.
- (6) Schukraft, G. E. M.; Ayala, S.; Dick, B. L.; Cohen, S. M. Isoreticular Expansion of PolyMOFs Achieves High Surface Area Materials. *Chem. Commun.* **2017**, *53*, 10684–10687.
- (7) Guillermin, V.; Ragon, F.; Dan-Hardi, M.; Devic, T.; Vishnuvarthan, M.; Campo, B.; Vimont, A.; Clet, G.; Yang, Q.; Maurin, G.; Férey, G.; Vittadini, A.; Gross, S.; Serre, C. A Series of Isoreticular, Highly Stable, Porous Zirconium Oxide Based Metal-Organic Frameworks. *Angew. Chemie - Int. Ed.* **2012**, *51*, 9267–9271.
- (8) Dubbeldam, D.; Krishna, R.; Calero, S.; Yazaydin, A. Ö. Computer-Assisted Screening of Ordered Crystalline Nanoporous Adsorbents for Separation of Alkane Isomers. *Angew. Chemie - Int. Ed.* **2012**, *51*, 11867–11871.
- (9) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers

- in a Metal-Organic Framework with Triangular Channels. *Science*. **2013**, *340*, 960–964.
- (10) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069.
- (11) Sun, Y.; Zhou, H. C. Recent Progress in the Synthesis of Metal-Organic Frameworks. *Sci. Technol. Adv. Mater.* **2015**, *16*, 054202.

6 SEPARATION OF PENTANE AND HEXANE ISOMERS BY A SYNERGISTIC ACTION OF MOF MIL-160(Al) AND ZEOLITE 5A

The content of this chapter is based on:¹

- (1) Brântuas, P. F.; Henrique, A.; Wahiduzzaman, M.; Von Wedelstedt, A.; Maity, T.; Rodrigues, A. E.; Nouar, F.; Lee, U.-H.; Cho, K. H.; Maurin, G.; Silva, J. A. C.; Serre, C. Separation of Branched Alkane Feeds by a Synergistic Action of Zeolite and Metal-Organic Framework. *Adv. Sci.* **2022**, 2201494.

Henrique, A.; Brântuas, P. F.; Rodrigues, A. E.; Silva, J. A. C. Adsorption Dynamics of Pentane and Hexane Isomers in the microporous Metal-Organic Framework MIL-160(Al) and in a mixed-bed of MIL-160(Al) and Zeolite 5A. To be submitted.

Zeolites and MOFs have frequently been considered “*competitors*” for the development of new advanced separation processes. Herein we demonstrate how an unprecedented synergistic action of two complementary benchmark materials of each family of porous solids, a commercially available zeolite 5A and the bio-derived Al-dicarboxylate MOF MIL-160(Al), leads to a novel adsorptive process for octane upgrading of gasoline through an efficient separation of alkane isomers into HRON and LRON fractions. This innovative mixed-bed adsorbent strategy encompasses a thermodynamically-driven separation of hexane isomers according to the degree of branching by MIL-160(Al) coupled to a steric rejection of pentane and hexane branched isomers by the molecular sieve zeolite 5A. The adsorptive separation ability of this MOF/zeolite duo was further evaluated under industrial working conditions by breakthrough and continuous cyclic experiments with a mixed-bed of shaped adsorbents. Remarkably, at the industrially relevant temperature of 423 K, an ideal sorption hierarchy of LRON over HRON alkanes is achieved, i.e., nC6 >> nC5 >> 2MP > 3MP >>> 23DMB > iC5 $\approx$ 22DMB, associated with an exceptional 92 RON ideal productivity of 1.14 mol.dm⁻³, which corresponds to a substantial leap-forward when compared with existing processes. The breakthrough data of this thermodynamically driven separation has been satisfactorily simulated using the DSL and Langmuir isotherms that conveniently fitted the multicomponent adsorption equilibrium in MIL-160(Al) and zeolite 5A, respectively. From the numerical simulations, equal k_{LDF} coefficients for the alkane isomers in MIL-160(Al) (ca. 0.00857 - 0.0156 s⁻¹) and for the linear paraffins in zeolite 5A (ca. 0.00354 - 0.00556 s⁻¹) were found.

6.1 Introduction

In this chapter, a novel adsorptive process for octane upgrading of gasoline through an efficient separation of pentane and hexane isomer mixtures into fractions of LRON and HRON compounds is proposed. Such process relates to the use of aluminium 2,5-furandicarboxylate microporous MOF, namely MIL-160(Al), featuring a general formula $\text{Al}(\text{OH})[\text{O}_2\text{C}-\text{C}_4\text{H}_2\text{O}-\text{CO}_2]$. The material has already shown promise for potential applications such as heat reallocation (to find new compounds for heat transfer applications),²⁻⁴ CO_2 capture in pre- and post-combustion conditions,⁵ among others.⁶⁻⁸

MIL-160(Al), whose structure is isostructural to that of the Al isophthalate CAU-10(Al),⁹ is built up from helical *cis* corner-shaping chains of $\text{AlO}_4(\text{OH})_2$ octahedra connected via five-membered ring 2,5-furandicarboxylate groups (FDCA) as linker, Figure 6.1. All the octahedra are surrounded by oxygen atoms from four linkers and two hydroxyl groups. The $-\text{OH}$ ions are in *cis*- position and bridge the Al centres to create chains. This leads to the formation of helical chains that run along the c-axis. The linkers are connected to four octahedra from two chains together. The resulting 3D framework exhibits square-shaped sinusoidal one-dimensional microporous channels of free aperture ranging from 0.4 to 0.6 nm in diameter.^{2,5}

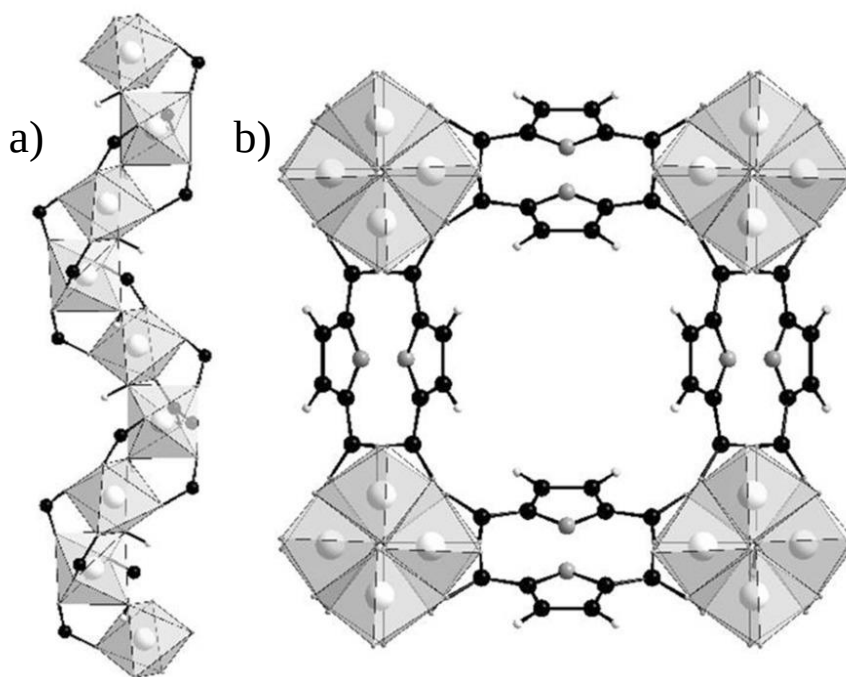


Figure 6.1 | Schematic view of MIL-160(Al): a) chains *cis*-connected by corner and surrounded by four carboxylates from four linkers, and **b)** square-shaped channels delimited via the linkers connecting four chains. Metal polyhedra, carbon, oxygen, and hydrogen atoms are in light grey, black, grey, and white, respectively. Adapted from the ref. 2

Regarding physical properties, MOF MIL-160(Al) has a BET surface area and micropore volume of $1070 \pm 20 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.398 \pm 0.005 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively, as reported by Cadiau et al.² while Permyakova et al.³ stated a value of $0.46 \text{ cm}^3 \cdot \text{g}^{-1}$ for the pore volume. In addition, the concomitant presence of weak Bronsted-acidic –OH sites and a heterocyclic ring within narrow pores leads to a highly hydrophilic character to the MOF material.³

This MOF was deliberately selected for such an ambitious target due to its inherent many attractive features:

- 1) the bio-sourced linker (FDCA) issued from the oxidation of 5-(hydroxymethyl)furan-2-carbaldehyde (HMF), a fructose-based material that is considered by the bioplastic industry to produce polyethylene furanoate, could potentially make this MOF a low-cost;^{10,11}
- 2) a safe and green ambient pressure method in line with a facile industrial production (effluent pre-treatment is not required, given the non-toxic and non-corrosive character of the materials);¹²
- 3) its chemical and thermal robustness;^{2,3}
- 4) its microporous channels with pore size ranging from 0.4 to 0.6 nm that are suitable for the separation of small organic molecules.⁵

In separation processes, shaped adsorbent materials with the appropriate particle size and density are a practical prerequisite for commercialization. The shaped particles, which usually contain a few wt.% of an inorganic or polymeric binder, shall also maintain the adsorption properties of the powder. Knowing that MIL-160(Al) can be produced at a multi-kilogram scale with a predicted low-cost industrial production,¹² we aimed to evaluate the adsorption dynamics of all pentane and hexane isomers in shaped MIL-160(Al).

The first section of this chapter, Section 6.2, describes the structural and physical properties of the shaped materials, MIL-160(Al) and zeolite 5A, by different characterization techniques, including MIP, N₂ sorption isotherms, and SEM. In Section 6.3, the experimental and numerical results are shown. First, single component isotherms of all pentane and hexane isomers in MIL-160(Al), in a wide range of temperature and alkane partial pressures, are presented. Then, experiments with multicomponent mixtures are explored at a constant total alkane pressure and different temperatures. Initially, breakthrough curves with quinary mixtures of all hexane isomers and septenary mixtures of all pentane and hexane isomers are given at a constant total alkane pressure and different temperatures. Thereafter, the synergistic

action of a mixed-bed made by MOF MIL-160(Al) and the commercially available zeolite 5A is shown through breakthrough curves with septenary mixtures of all alkane isomers. Finally, preliminary PSA experiments evaluate the MOF/zeolite duo mixed-bed under cyclic operation. The equilibrium data from single and multicomponent breakthrough curves are modelled by the DSL (MIL-160(Al)) and Langmuir (zeolite 5A) isotherms, and fitted parameters used in the dynamic mathematical model for the numerical simulations are also shown. To conclude, a summary of the key findings of the chapter is given in Section 6.4.

6.2 Materials and methods

The MIL-160(Al) used in this work was provided by the *Korea Research Institute of Chemical Technology (KRICT)*. It is in the shaped form of beads with a diameter ranging from 2.0 to 3.35 mm (Figure 6.2a). The material was produced through a wet granulation route using an inorganic binder (silica sol solution 10 wt.%) following a previously reported protocol.³

The zeolite 5A was supplied by *CWK Chemiewerk Bad Köstritz GmbH* and has the commercial name *KÖSTROLITH® 5A BFK*. It is in the shaped form of binder-free beads and possesses a diameter range between 1.2 to 2.0 mm (Figure 6.2b). The material was manufactured through an advanced synthesis, in which the binder (metakaolin) is itself transformed into zeolite matter, overcoming the loss in adsorption capacity associated with the binder composite.^{13,14}

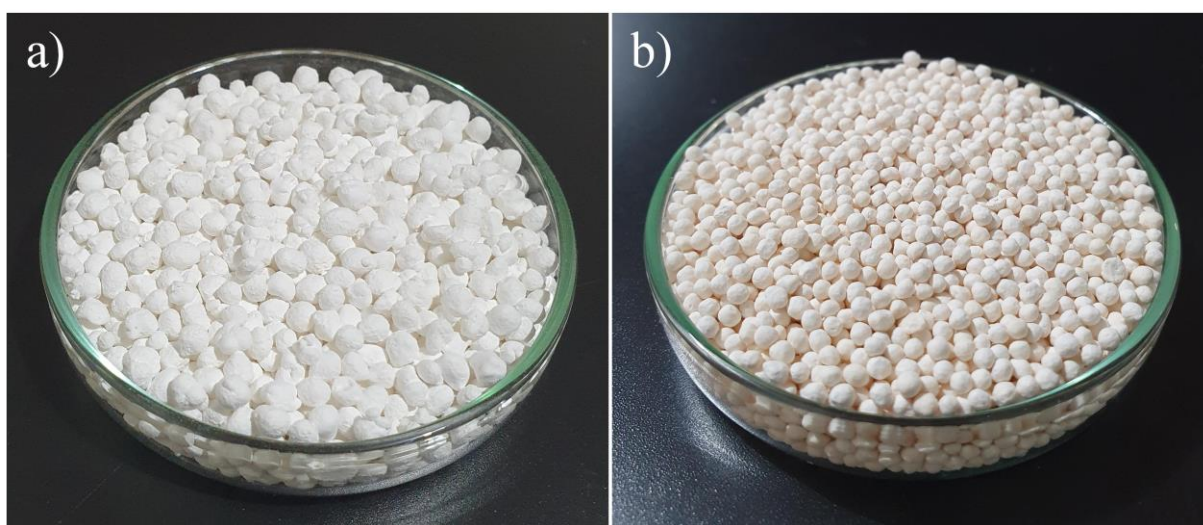


Figure 6.2 | Photo records of adsorbent materials: a) MIL-160(Al) beads and b) zeolite 5A binder-free beads.

The structural and textural properties of both materials were evaluated by a range of characterization techniques, in which their porous nature, surface area, and surface morphology were accessed through MIP, N₂ physisorption isotherms, and SEM analysis, respectively. Most characterization studies were performed at the *Laboratorio de Sólidos Porosos* of the *University of Málaga*, except data from MIP for the MIL-160(Al), which was measured at *KRICT*.

6.2.1 Porosimetry by Hg Intrusion of MIL-160(Al) and Zeolite 5A

The meso- and macroporosity of the shaped materials were evaluated by MIP using a pore size analyser (*AutoPore IV 9500* (MIL-160(Al)) and *AutoPore V 9600* (Zeolite 5A), *Micromeritics*), applying a contact angle of 130° and covering the pressure range between 1.6×10^{-3} to 2.3×10^2 MPa. Before the experiments, the samples (≈ 350 mg) were outgassed at 423 K for 12 h under a vacuum atmosphere. Figure 6.3 shows the results of the Hg intrusion tests. As it can be seen, MIL-160(Al) (Figure 6.3a) presents a heterogeneous macropore size distribution, with pores in the range of $5.5 \times 10^0 - 4 \times 10^1$ nm, $5.0 \times 10^1 - 7.0 \times 10^2$ nm (centred at 1.6×10^2 nm), and $1.0 \times 10^5 - 8.0 \times 10^5$ nm. In contrast, zeolite 5A (Figure 6.3b) has a homogeneous pore size distribution where a large amount of macropores is seen, with a maximum centred at 5.8×10^2 nm. The peaks identified on both materials correspond to interparticle voids between the individual crystals in the shaped beads. Regarding the cumulative pore volume curves, the Hg uptake increases as the pore size decrease, i.e., increase of Hg intrusion pressure.

Information on the total intrusion volume, total pore area, median pore diameter (volume and area), average pore diameter (4V/A), apparent density, solid density, and porosity is given in Table 6.1. The apparent densities of the beads were determined at the lowest pressure (1.6×10^{-3} MPa for MIL-160(Al) and 3.6×10^{-3} MPa for zeolite 5A), at which Hg does not spontaneously penetrate the pores and only surrounds the particles without wetting them. On the other hand, the solid densities were obtained at the highest pressure (2.3×10^2 MPa for MIL-160(Al) and 2.1×10^2 MPa for zeolite 5A), at which Hg is forced into the meso- and macropores (except into the micropores), filling the majority of the open secondary pore system generated during the shaping process.

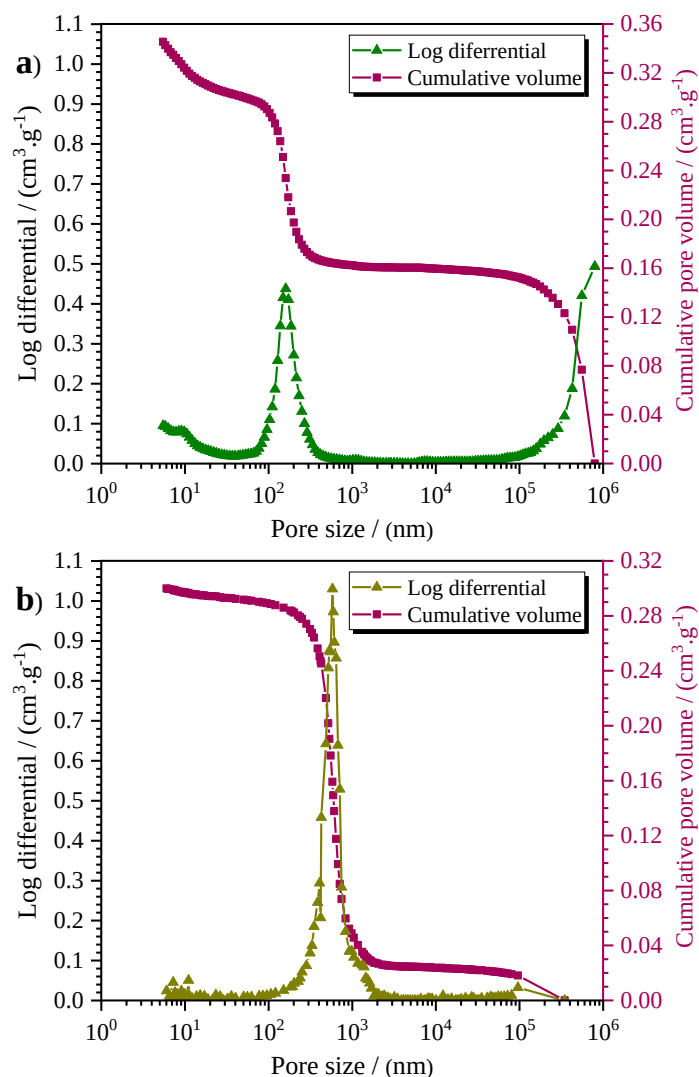


Figure 6.3 | Macroscopic pore size and cumulative pore volume distribution of adsorbent materials: a) MIL-160(Al) and b) zeolite 5A.

Table 6.1 | Textural properties of MIL-160(Al) and zeolite 5A determined by MIP.

Hg porosimetry data			
		MIL-160(Al)	Zeolite 5A
Total intrusion volume	$(\text{cm}^3 \cdot \text{g}^{-1})$	0.345	0.300
Total pore area	$(\text{m}^2 \cdot \text{g}^{-1})$	21.4	4.90
Median pore diameter (volume)	(nm)	294	593
Median pore diameter (area)	(nm)	9.10	24.6
Average pore diameter (4V/A)	(nm)	64.6	245
Apparent density	$(\text{g} \cdot \text{cm}^{-3})$	0.903	1.17
Solid density	$(\text{g} \cdot \text{cm}^{-3})$	1.31	1.80
Porosity	(%)	31.2	35.1

6.2.2 Adsorption and Desorption Isotherms of MIL-160(Al) and Zeolite 5A

Gas sorption measurements were performed to give insight into the surface area of the shaped materials. N₂ adsorption and desorption isotherms were measured in an accelerated surface area and porosimetry system (ASAP® 2420, Micromeritics), at a temperature of 77 K and a pressure range of 2.5 – 10⁵ Pa. Before the experiments, the samples (≈350 mg) were outgassed at 423 K for 12 h under a vacuum atmosphere. The corresponding adsorption equilibrium isotherms are given in Figure 6.4. As it shows, they are marked as type I according to the updated IUPAC classification, with their shape being concave to the x-axis, a typical characteristic of microporous materials.¹⁶ The steep uptake at a very low relative pressure (p/p_0 between 10⁻⁵ to 10⁻²) is related to enhanced gas-solid interactions in narrow pores, resulting in pore filling, in which the loading progressively increases up to ≈225 and 170 cm³.g⁻¹ for MIL-160(Al) and zeolite 5A, respectively. In addition, in the MIL-160(Al) material, a slight increase in the N₂ uptake (≈255 cm³.g⁻¹) is observed at a high relative pressure (p/p_0 between 0.7 to 1), suggesting its adsorption on a small amount of macropores. Comparing the two branches of the isotherms, it is possible to assume that practically there is no hysteresis loop, suggesting that the adsorption process is completely reversible for both materials.

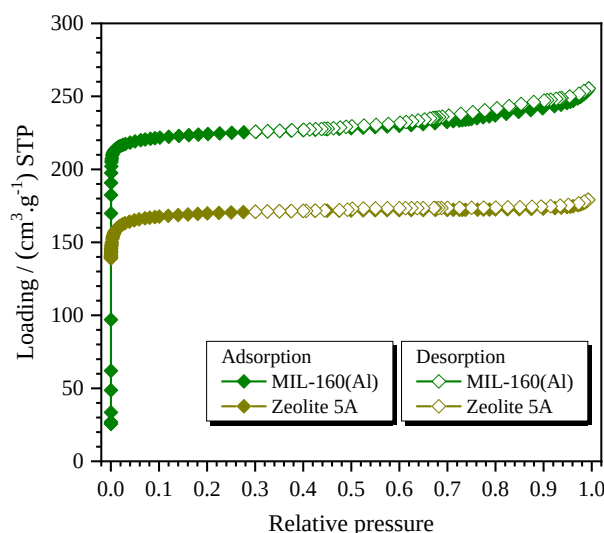


Figure 6.4 | N₂ adsorption and desorption isotherms at 77 K of MIL-160(Al) and zeolite 5A.

The textural properties of MIL-160(Al) and zeolite 5A, derived from the N₂ sorption measurements, such as specific surface area (S_{Langmuir}) estimated using the Langmuir method, both external surface area, microporous surface area, and micropore volume determined by the t -method, and the total pore volume calculated at $p/p_0 \approx 0.95$ are summarised in Table 6.2.

Table 6.2 | Textural properties of MIL-160(Al) and zeolite 5A determined by N₂ sorption measurements.

N ₂ adsorption data			
		MIL-160(Al)	Zeolite 5A
S_{Langmuir}	(m ² .g ⁻¹)	986	748
External surface area	(m ² .g ⁻¹)	27.5	5.73
Microporous surface area	(m ² .g ⁻¹)	959	742
Micropore volume	(cm ³ .g ⁻¹)	0.335	0.262
Total pore volume	(cm ³ .g ⁻¹)	0.380	0.269

6.2.3 SEM Analysis of MIL-160(Al) and Zeolite 5A

To study the surface morphology of the shaped materials, a scanning electron microscopy instrument with high resolution (*JSM-6490, JEOL*) was used. The obtained images showing the characteristic dimension of the beads and their specific crystal appearance at different scales and magnifications are displayed in Figures 6.5 and 6.6, for MIL-160(Al) and zeolite 5A, respectively, showing that both materials are highly crystalline.

The SEM images of MIL-160(Al) confirm the preservation of the crystal shape after the granulation process. Crystals displaying a cubic morphology with distinct edges and points, with sizes ranging from 1.0 to 1.5 μm. Moreover, the crystals exhibit a granular surface, which is consistent with the presence of silica particles at the external surface of MIL-160(Al) particles. Nevertheless, they are presumed not to be involved in strong interfacial interactions.³

Results for the zeolite 5A reveal that they also present a characteristic cubic morphology, with a crystal diameter ranging from 1.0 to 2.0 μm. However, some intergrowth between the original crystals in the single shape can be observed, which results from the conversion of the metakaolin into an irregularly polycrystalline zeolite matter, and by the way, forming the macropores.¹⁴

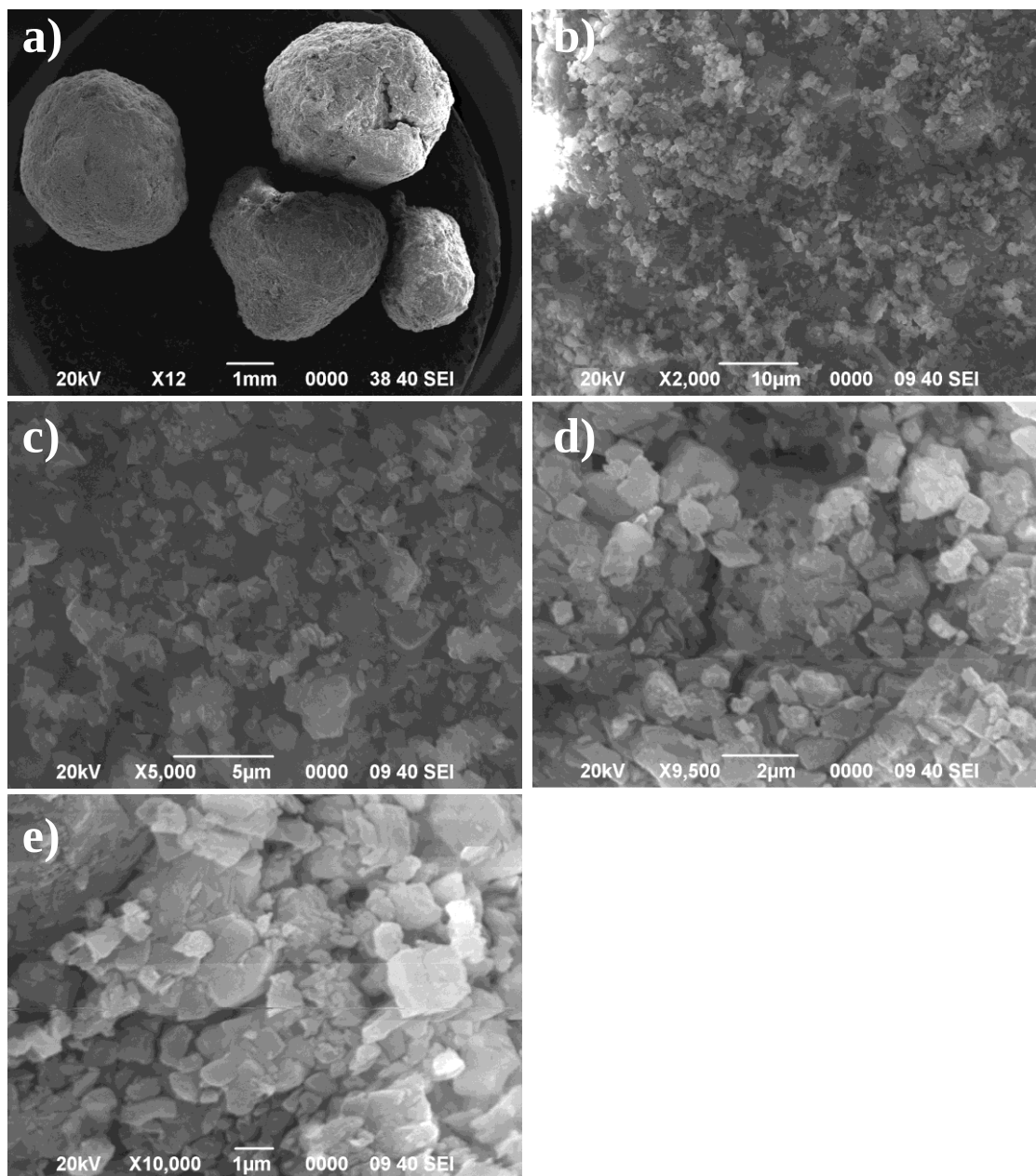


Figure 6.5 | SEM images of MIL-160(Al) at different scales and magnifications: a) x12, b) x2000, c) x5000, d) x9500, and e) x10000.

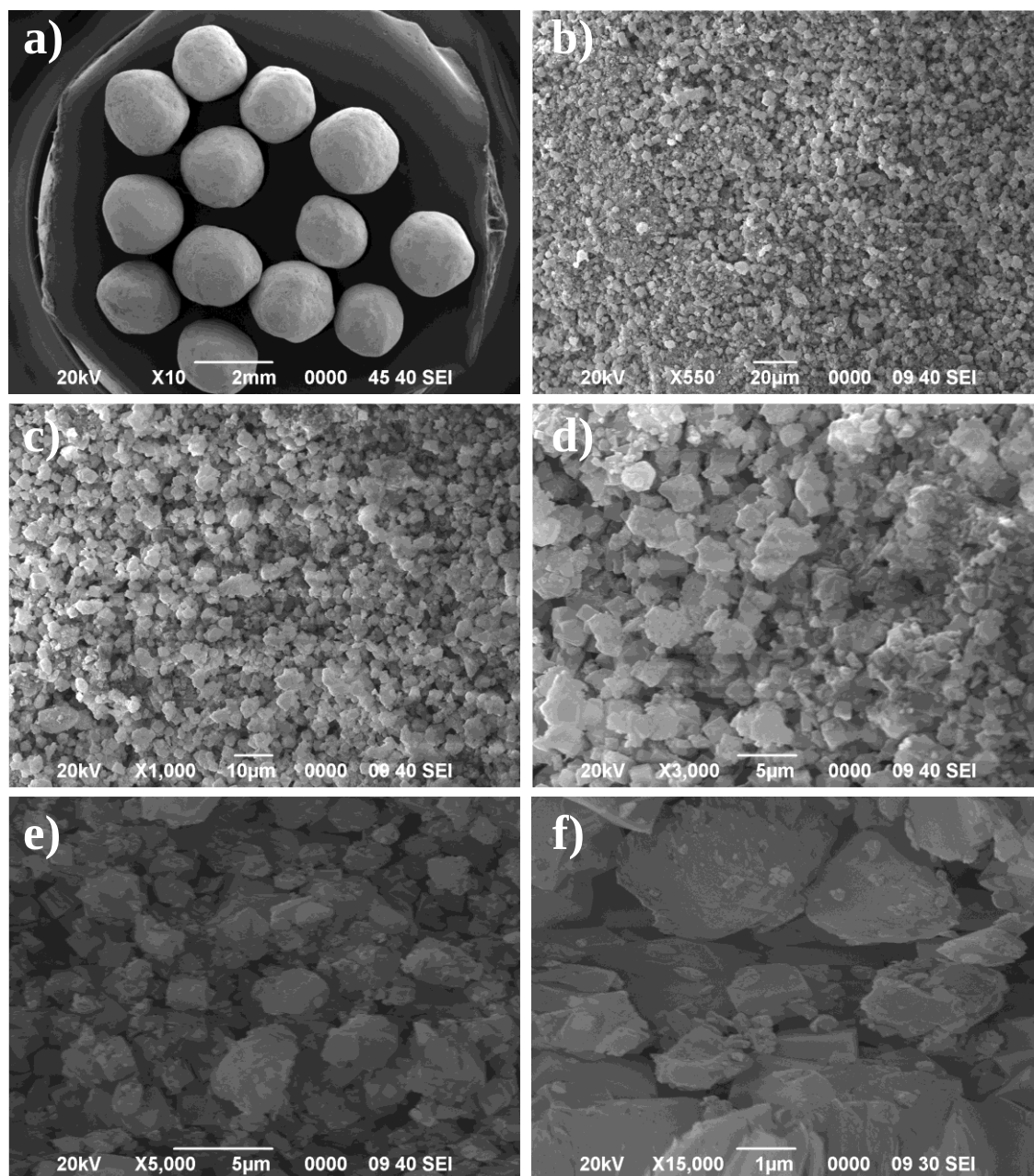


Figure 6.6 | SEM images of zeolite 5A at different scales and magnifications: a) x10, b) x550, c) x1000, d) x3000, e) x5000, and f) x15000.

6.3 Results and Discussion

6.3.1 Single Component Adsorption of Pentane and Hexane Isomers in MIL-160(Al)

Single component adsorption equilibrium isotherms of all pentane and hexanes isomers in MIL-160(Al) were determined from breakthrough experiments performed at three different temperatures, 373, 423, and 473 K, and with alkane partial pressure up to 50 kPa (balance with He to setting a total pressure in the column of 101.3 kPa). Complete information on the experimental fixed bed runs performed, including the flow rates of alkane and He, and the equilibrium loadings, are reported in Table 6.3.

From Table 6.3, one can see that the equilibrium loadings for all components are thermodynamically consistent since they increase as the alkane partial pressure increases (at a constant temperature) and decrease as the temperature increases (at a constant alkane partial pressure). Whatever the temperature studied, the linear nC6 is the guest molecule that presents a higher affinity with the MIL-160(Al) material, with loadings going up to 1.80 mol.kg⁻¹ (run 1_6), which is around 20% higher than its maximum loading capacity in pellets of zeolite 5A (1.50 mol.kg⁻¹).¹⁶ Moreover, in contrast to zeolite 5A, which behaves as a molecular sieve for separating linear from branched paraffins, the dimensions of the channels in MIL-160(Al) are sufficiently large to accommodate all the alkanes, meaning that their sorption is governed by equilibrium and is dependent on the structure and adsorptive properties of the individual molecules within the MOF channels.

Analysing the pentane and hexane isomers separately, one can observe that the higher the branching degree, the lower the uptake. The adsorption equilibrium hierarchy in MIL-160(Al) always fits the following trend: nC5 > iC5 and nC6 > 2MP > 3MP > 23DMB > 22DMB, respectively, being similar to their normal boiling point order. The global adsorption hierarchy for the seven components is: nC6 > 2MP > 3MP > nC5 > 23DMB > iC5 > 22DMB, which differs from the ideal one (LRON over HRON) due to the presence of linear nC5 between the mono-branched 3MP and di-branched 23DMB hexanes.

Table 6.3 | Experimental conditions for measuring single component breakthrough curves of pentane and hexane isomers in MIL-160(Al) and results.¹⁷

Run	Temp. (K)	Alkane partial pressure (kPa)	Alkane flow rate ($\mu\text{mol}.\text{min}^{-1}$)	He flow rate ($\text{mL}.\text{min}^{-1}$)	iC5	nC5	22DMB	23DMB	3MP	2MP	nC6
<i>Single component: pentane and hexane isomers</i>											
1_1	373	2.50	12.2	10.8		0.873	0.677	0.733	0.999	1.11	1.24
1_2	373	5.00	24.3	10.5	0.784	1.09	0.753	0.909	1.15	1.28	1.32
1_3	373	10.0	48.6	9.93	1.01	1.25	0.939	1.17	1.33	1.40	1.47
1_4	373	20.0	97.2	8.83	1.29	1.42	1.10	1.34	1.55	1.60	1.66
1_5	373	30.0	146	7.73	1.48	1.54	1.18	1.45	1.64	1.67	1.70
1_6	373	50.0	243	5.52	1.58	1.63	1.29	1.49	1.67	1.75	1.80
2_1	423	2.50	10.7	9.49		0.292	0.170	0.229	0.366	0.471	0.579
2_2	423	5.00	21.4	9.25	0.263	0.440	0.263	0.403	0.519	0.656	0.721
2_3	423	10.0	42.9	8.76	0.431	0.653	0.405	0.529	0.716	0.779	0.899
2_4	423	20.0	85.7	7.79	0.599	0.821	0.575	0.712	0.908	0.990	1.10
2_5	423	30.0	129	6.81	0.733	0.929	0.675	0.819	0.983	1.07	1.19
2_6	423	50.0	214	4.87	0.922	1.09	0.805	0.955	1.14	1.22	1.28
3_1	473	2.50	9.58	8.49	0.0273	0.0508	0.0416	0.0610	0.0757	0.131	0.156
3_2	473	5.00	19.2	8.27	0.0609	0.143	0.0604	0.0967	0.125	0.201	0.255
3_3	473	10.0	38.3	7.83	0.130	0.223	0.130	0.167	0.238	0.290	0.394
3_4	473	20.0	76.7	6.96	0.214	0.344	0.205	0.313	0.424	0.498	0.561
3_5	473	30.0	115	6.09	0.321	0.442	0.273	0.390	0.579	0.603	0.705
3_6	473	50.0	192	4.35	0.435	0.529	0.363	0.482	0.685	0.728	0.822

The mass of MIL-160(Al) used in the experiments was 2.81 g, packed in a column with a 100 mm length and 8 mm internal diameter;

The flow rates are expressed at STP conditions;

This set of single component experiments was performed by Ivan M. C. Pinto, and the breakthrough curves can be seen elsewhere.¹⁷

The adsorption equilibrium isotherms are shown in Figure 6.7 (pentane isomers) and 6.8 (hexane isomers). It can be seen that all of them are of type I according to IUPAC classification.¹⁵ At 373 K, the profiles for most alkanes show a pronounced rectangular shape where the saturation capacity is almost reached, and the equilibrium data nearly approaches a horizontal plateau (from alkane partial pressures above 30 kPa). Therefore, in principle, the maximum adsorption capacity should not differ too much from the loadings obtained at 50 kPa. Increasing the temperature, the degree of steepness decreases, and the isotherms become smoother, indicating a decrease in the adsorbate-adsorbent interactions.

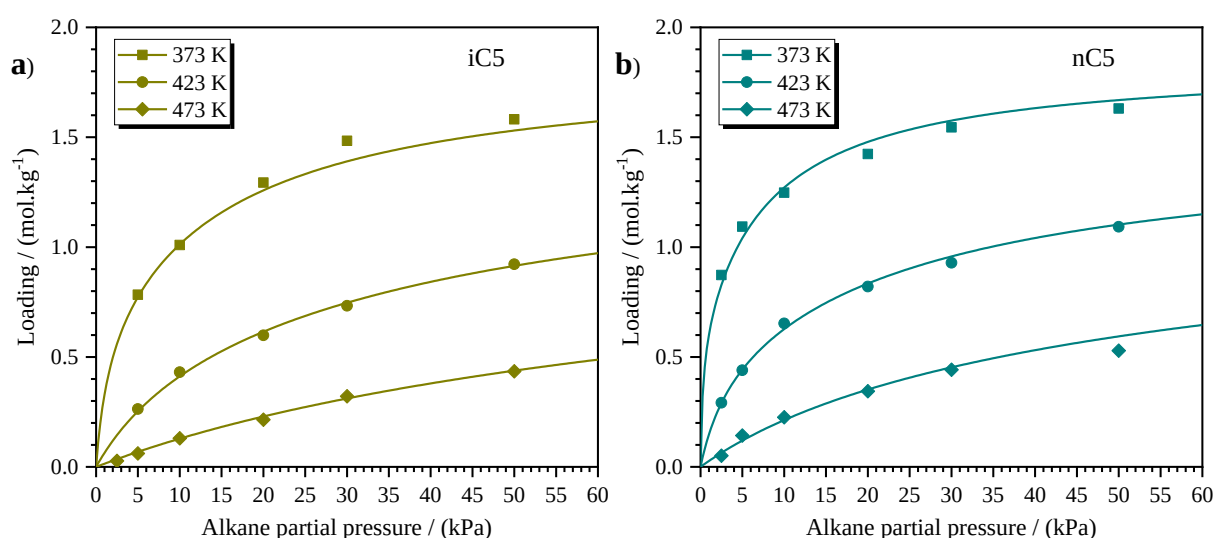


Figure 6.7 | Single component adsorption equilibrium isotherms of pentane isomers in MIL-160(Al): a) iC5 and b) nC5. The continuous lines represent the DSL model predictions.

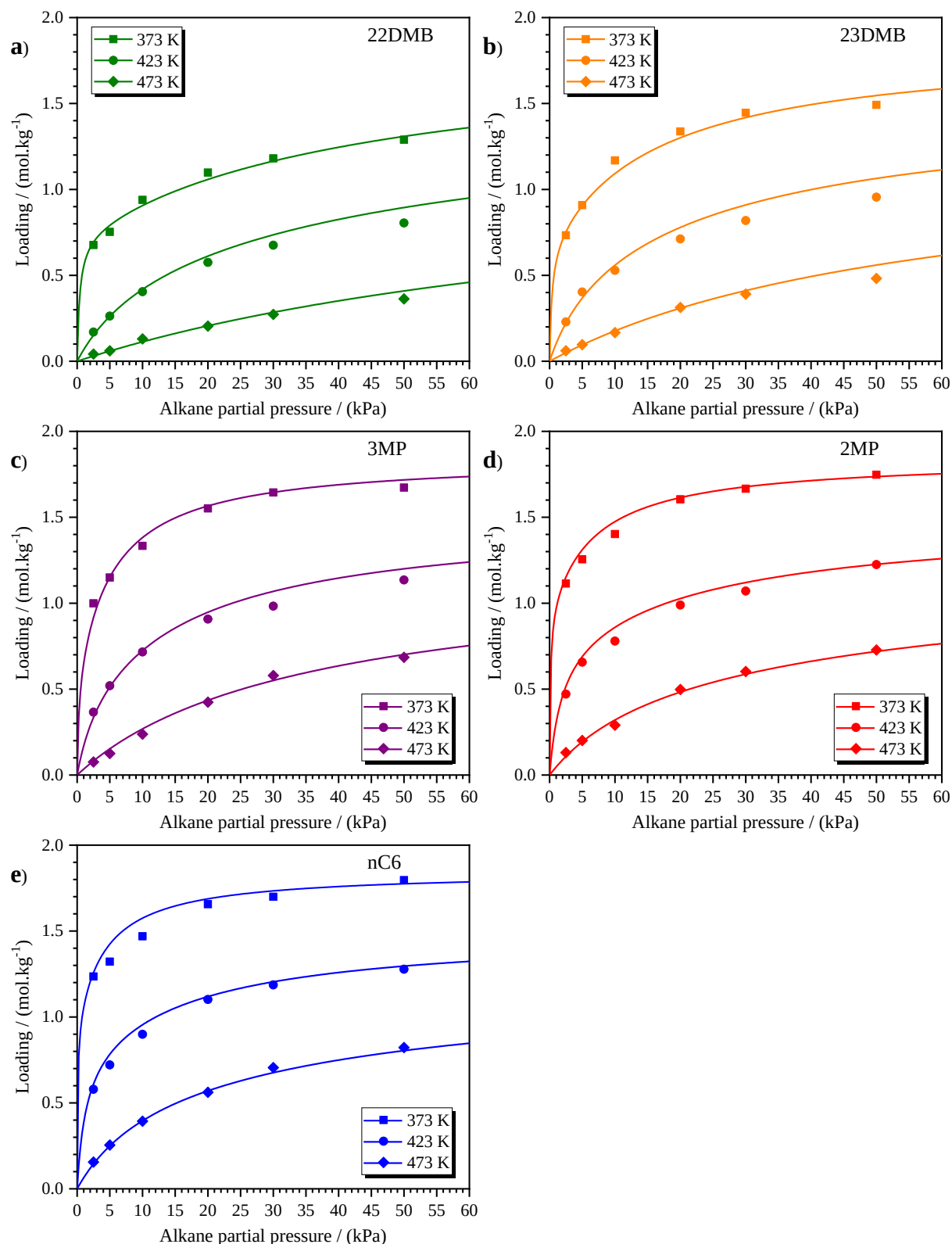


Figure 6.8 | Single component adsorption equilibrium isotherms of hexane isomers in MIL-160(Al): a) 22DMB, b) 23DMB, c) 3MP, d) 2MP, and e) nC6. The continuous lines represent the DSL model predictions.

6.3.2 Multicomponent Adsorption of Pentane and Hexane Isomers in MIL-160(Al) and Zeolite 5A

Studies with multicomponent equimolar mixtures were conducted to gain further insight into the adsorption behaviour of pentanes and hexane isomers in MIL-160(Al). Firstly, we addressed breakthrough curves with quinary mixtures of all five hexane isomers (nC6/2MP/3MP/23DMB/22DMB). Then, the pentane isomers were incorporated into the system, and breakthrough experiments with a feed mixture containing all the pentane and hexane isomers (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB) were further performed. Thereafter, the septenary studies were again considered, but in a mixed-bed of MIL-160(Al) and zeolite 5A, in which breakthroughs were measured followed by preliminary simple cyclic PSA experiments.

6.3.2.1 Multicomponent Adsorption of Hexane Isomers

The quinary breakthrough experiments were performed at the temperatures of 423 and 473 K and total alkane pressure of 50 kPa, relevant to the industrial separation conditions. Table 6.4 summarizes all experimental conditions applied, the component loadings, the ideal productivities, and the selectivities for each run performed. One can observe that the mixture loading follows the same thermodynamic consistency observed in single component experiments.

The breakthrough curves shown in Figure 6.9 reveal the outstanding property of the material to separate the hexane isomers into valuable fractions according to the degree of branching. For both temperatures, the results show that the HRON di-branched hexanes 22DMB and 23DMB elute first, and they are completely separated from the LRON mono-branched 3MP and 2MP while the LRON linear nC6 elutes much later. Notably, the sorption hierarchy of hexane isomers is $\text{nC6} \gg 2\text{MP} \approx 3\text{MP} \gg 23\text{DMB} > 22\text{DMB}$, being in close agreement with the single component experiments. The shape of the breakthrough curves for each isomer clearly indicates that this excellent segregation of the mixture and selectivity in MIL-160(Al) is primarily based on thermodynamically equilibrium competition due to their steepness and overshoot phenomenon. The least adsorbed components (moving faster in the column) are pushed out from the adsorbent by the more strongly adsorbed ones (moving slower in the column), and therefore their concentration sequentially rises above the feed.

Table 6.4 | Experimental conditions for measuring breakthrough curves for equimolar mixtures of pentane and hexane isomers in MIL-160(Al), in a mixed-bed of MIL-160(Al)/zeolite 5A, and results.

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol.min}^{-1}$)	He flow rate (mL.min^{-1})	q_i (mol.kg^{-1})							q_{mix} (mol.kg^{-1})	P_s RON 92 (mol.dm^{-3})	S_s
					iC5	nC5	22DMB	23DMB	3MP	2MP	nC6			
Quinary mixture: MIL-160(Al)														
4_1	423	50.0	281	6.39	-	-	0.0572	0.116	0.328	0.378	0.542	1.42	1.02	7.20
4_2	473	50.0	252	5.71	-	-	0.0445	0.0868	0.183	0.203	0.278	0.795	0.460	5.06
Septenary mixture: MIL-160(Al)														
5_1	423	50.0	563	12.8	0.0844	0.187	0.0763	0.120	0.282	0.315	0.442	1.51	0.590	-*
5_2	473	50.0	503	11.4	0.0586	0.113	0.0536	0.0853	0.162	0.179	0.240	0.891	0.263	-*
Septenary mixture: MIL-160(Al) + Zeolite 5A														
6_1	423	50.0	563	12.8	0.0821	0.247	0.0805	0.135	0.317	0.356	0.623	1.84	1.14	5.18
6_2	473	50.0	503	11.4	0.0400	0.160	0.0439	0.0764	0.163	0.173	0.388	1.04	0.644	5.51

The mass of MIL-160(Al) used in the single bed experiments was 16.5 g, packed in column 3 (see Chapter 3);

The mass of MIL-160(Al) and zeolite 5A used in the mixed-bed experiments was 12.8 g and 5.49 g, respectively, packed in column 3;

The flow rates are expressed at STP conditions;

* The elution order (sorption hierarchy) from these experiments does not fit with the one from Eq.3.5 (see Chapter 3).

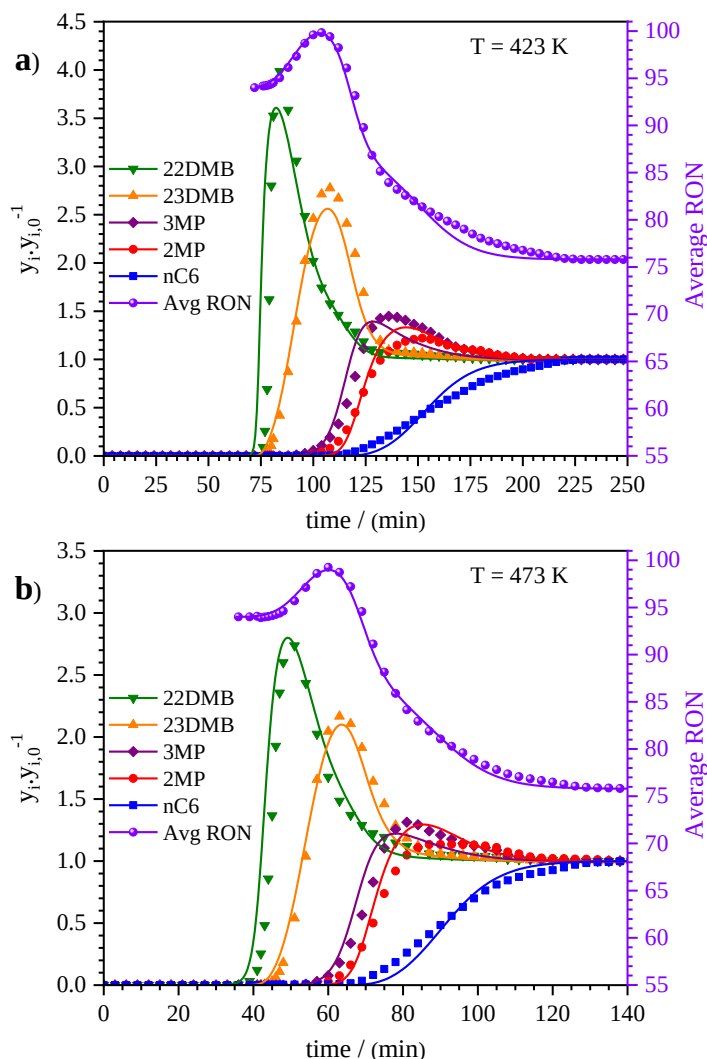


Figure 6.9 | Experimental and numerical breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-160(Al) at 50 kPa: a) 423 K, b) 473 K. The continuous lines represent the numerical simulations.

Figure 6.9 also shows the real-time RON of the product mixture leaving the column (right y-axis) from where it can be read a value around 99 when only 22DMB and 23DMB elute from the column separated from the other isomers. Moreover, at 423 K, the calculated 92 RON ideal productivity is $1.02 \text{ mol} \cdot \text{dm}^{-3}$, which is approximately two times higher than that reported for the benchmark MOF $\text{Fe}_2(\text{BDP})_3$ ($0.54 \text{ mol} \cdot \text{dm}^{-3}$, obtained at 433 K and 100 kPa of total alkane pressure).¹⁸ The volumetric productivities were determined using the apparent density of the shaped beads, which is $0.903 \text{ g} \cdot \text{cm}^{-3}$ (Table 6.1). Also, these experiments further revealed that MIL-160(Al) maintains its selectivity performance under similar working conditions with the use of these shaped beads, while only a minimal decrease in the 92 RON ideal productivity was observed relative to an experiment performed with the material in the powdered form ($1.15 \text{ mol} \cdot \text{dm}^{-3}$). This result is important for further integration of this material in the industrial

process. More detailed information on the preliminary breakthrough experiments of hexane isomers in MIL-160(Al) powder can be consulted in the published version.¹

Another important remark is the fact that the separation by classes is kept at the highest temperature (Figure 6.9b) once the selectivity calculated from the ratio of the loadings between linear + mono-branched hexanes over the di-branched ones (5.06) is just slightly lower than that at 423 K (7.20). This means that the effect of temperature is practically the same for all hexane isomers, in which their elution time was reduced (loading capacity), but the selectivity between them did not significantly change.

CBMC simulations performed in a cooperation with *IGCM* were further considered to shed light on the microscopic mechanism at the origin of this notable separation performance of MIL-160(Al). Regarding the preferential sittings and conformations of each hexane isomer in the quinary mixture, the linear nC6 molecules are found to be aligned both along and across the MIL-160(Al) channel direction to favour interactions between the MOF pore wall and the largest fraction of the hexane skeleton. Thanks to their similar dimension and flexibility as nC6, the mono-branched isomers 2MP and 3MP can be equally aligned across the MIL-160(Al) channels, interacting with opposite pore walls and multiple furan linkers. However, associated with an adsorption affinity slightly lower than for nC6. In sharp contrast, the more compact di-branched isomers 23DMB and 22DMB are shorter and not flexible enough to adapt similar optimal arrangements, and only a small fraction of the carbon centres (1 or 2) effectively interacts with the MOF pore walls. This illustrates the weakening of the host/guest Van der Waals interactions with increasing degree of branching and the lower uptake of 22DMB and 23DMB in the quinary mixture. Complete information about the molecular simulation procedures and detailed analysis of obtained results can be found on the published version.¹

6.3.2.2 *Multicomponent Adsorption of Pentane and Hexane Isomers*

Screening tests with a septenary feed mixture containing all pentane and hexane isomers were further performed covering the same temperature range and total alkane pressure applied for the quinary breakthrough experiments. Detailed information on the experimental conditions and results are also reported in Table 6.4.

The breakthrough curves are shown in Figure 6.10. The sorption hierarchy was found as follows: of nC6 >> 2MP $\approx$ 3MP >> nC5 > 23DMB > iC5 $\approx$ 22DMB, also consistent with the

single component data. The presence of the iC5 and nC5 pentanes breaks the separation according to the degree of branching previously seen for the hexane isomers since both molecules elute nearly to the fraction of di-branched hexanes. However, from the point of view of the octane number improvement, it is advantageous that the HRON iC5 (93.5) leaves the adsorption column together with HRON 22DMB (94.0) and 23DMB (105) hexanes. Indeed, while the iC5 and 22DMB elute early — practically together — unwantedly, the LRON nC5 elutes later, almost simultaneously with the HRON 23DMB. This undesirable near-simultaneous elution leads to a substantial drop in the 92 RON ideal productivities. For example, at 423 K, a value of $0.59 \text{ mol}\cdot\text{dm}^{-3}$ is obtained, which is around 40% lower than that achieved for the separation of hexane isomers only ($1.02 \text{ mol}\cdot\text{dm}^{-3}$).

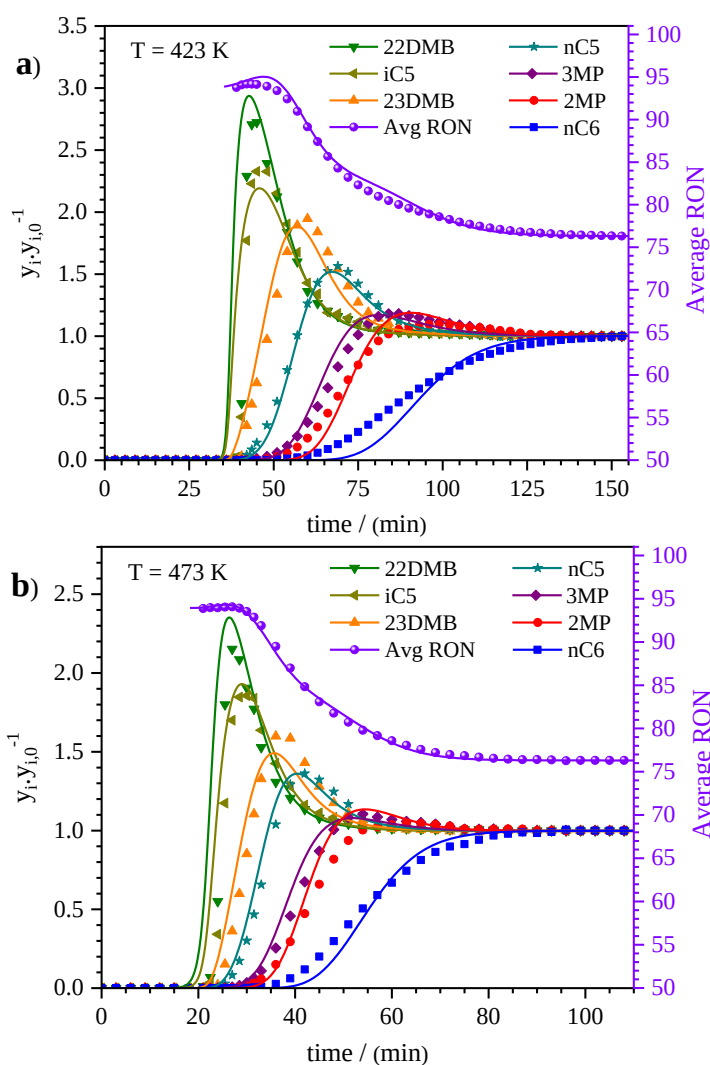


Figure 6.10 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in MIL-160(Al) at 50 kPa: a) 423 K, b) 473 K. The continuous lines represent the numerical simulations.

In order to see how the MIL-160(Al) behaves in the presence of only branched alkanes, an experiment in which the LRON normal alkanes (i.e., nC5 and nC6) were removed from the feed mixture was also performed in the preliminary set of breakthrough tests with the material in powdered form. Interestingly, the desired separation into two distinct fractions of HRON (22DMB $\approx$ iC5 < 23DMB) and LRON (3MP $\approx$ 2MP) paraffins is readily achieved (Figure 6.11). In this condition, at the early stage of the breakthrough, when only the 22DMB/iC5/23DMB components elute from the column, a maximum RON value of 97 is obtained. Noteworthy, as far as our knowledge goes, this is the first experimental evidence that an adsorbent effectively fractionates pentane and hexane branched isomers into two distinct HRON and LRON fractions.

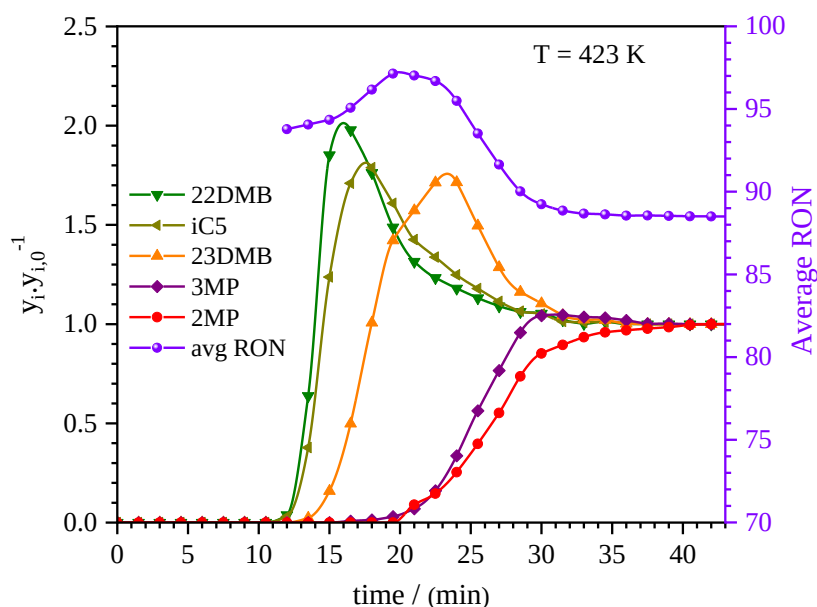


Figure 6.11 | Experimental breakthrough curves for a quinary equimolar mixture of pentane and hexane branched alkanes in MIL-160(Al) powder at 423 K and 50 kPa.

CBMC simulations were also performed for the mixtures of pentane and hexane isomers. The organization of all hexane molecules in the MIL-160 channel remains the same as observed for the equimolar hexane isomers mixture. The conformations of the mono-branched iC5 are rather similar to those of di-branched hexane isomers, while the linear nC5 molecules tend to adopt aligned configurations like nC6. However, its shorter length does not maximize the interactions with the pore walls.¹

6.3.2.3 Synergistic Action of MIL-160(Al) and Zeolite 5A to Separate all Pentane and Hexane Isomers into Classes of HRON and LRON Fractions

The results show in Figure 6.10 illustrate the difficulty of obtaining a high-octane value stream when MIL-160(Al) is used as the sole adsorbent material in cases of pentane/hexane isomers mixtures as fuel feed. Therefore, if one wishes to include all these alkanes into a single adsorption bed, one shall associate MIL-160(Al) with such adsorbent capable of performing the size-selective separation between linear and branched paraffins, based on their well-known differences in kinetic diameters, to remove nC5 from the overall branched pentanes/hexanes mixture. Then, as a next step, we deliberately chose to associate MIL-160(Al) with the commercially available zeolite 5A — known for its unique size-selective separation of linear/branched paraffins — to design a single adsorption bed able to feed all the pentane and hexane isomers and separate them into HRON and LRON fractions. Thus, septenary experiments were performed using a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A. Calculated results are also given in Table 6.4.

The corresponding experimental breakthrough data collected are shown in Figure 6.12 and clearly demonstrates the desired discrimination between fractions of HRON (22DMB, iC5, and 23DMB) and LRON (nC6, nC5, 2MP, and 3MP) alkanes. There is a change in the behaviour of nC5, which now leaves the column after 2MP and 3MP due to the presence of zeolite 5A that causes an increase in its time inside the bed, making it exit the column later than in the experiments done just with MIL-160(Al) (Figure 6.10). The ratio 70 wt.% MOF / 30 wt.% zeolite was selected in order to guarantee the complete displacement of the nC5 wavefront forward the mono-branched hexanes to obtain a pure fraction of only HRON molecules.

Figure 6.12 reveals an ideal sorption hierarchy $\text{nC6} \gg \text{nC5} \gg 2\text{MP} \approx 3\text{MP} \gg 23\text{DMB} > \text{iC5} \approx 22\text{DMB}$ associated with an excellent 92 RON ideal productivity of 1.14 mol.dm^3 (value calculated at 423 K). The volumetric productivities were determined using a weighted average between the apparent densities of MIL-160(Al) beads (0.903 g.cm^{-3}) and zeolite 5A binder-free beads (1.17 g.cm^{-3}) according to their amount in the mixed-bed, which resulted in a value of 0.983 g.cm^{-3} . Considering only the adsorption of linear alkanes on zeolite 5A, the nC6 presented higher loadings than nC5, as expected.^{18,19} Once more, the separation by classes is retained at the highest temperature, and the calculated selectivities for both breakthrough experiments are practically constant, it being 5.18 and 5.51, at 423K and 473K, respectively. In addition, these

values compare to the ones found in the experiments dealing with hexane isomers only (7.20 (423 K) and 5.06 (473K)).

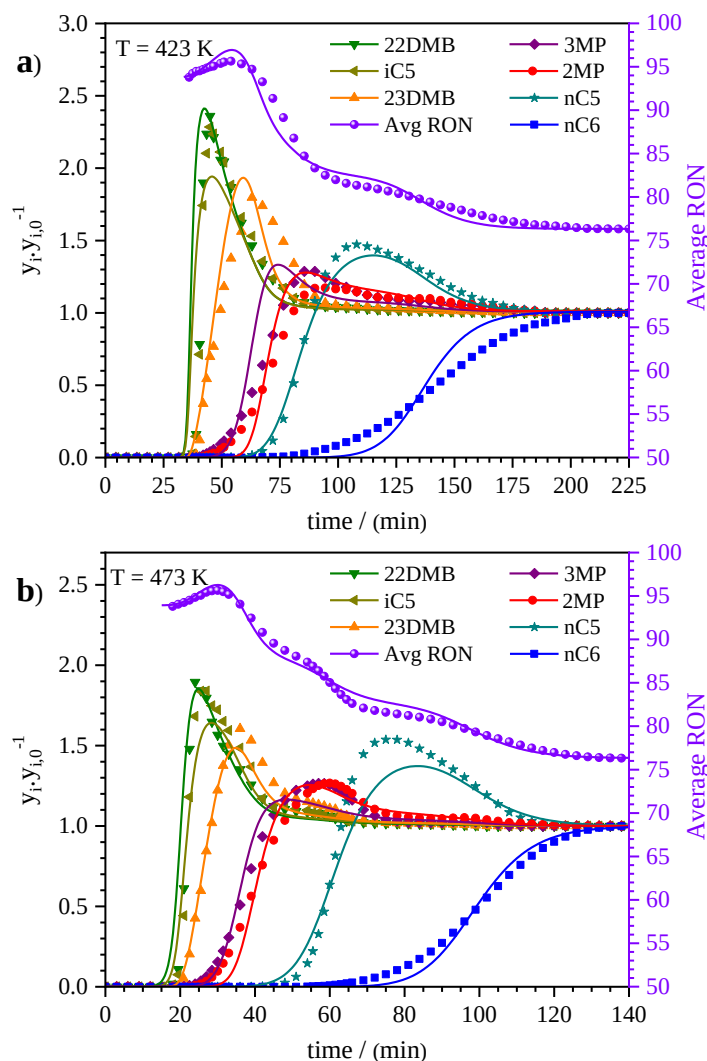


Figure 6.12 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 50 kPa: a) 423 K, and b) 473 K. The continuous lines represent the numerical simulations.

To see how these results could be relevant to industrial application, preliminary cyclic experiments were then carried out to prove that the MIL-160(Al)/zeolite 5A duo can be effective to upgrade the conventional TIP process under continuous cyclic adsorption operation. Information on the working conditions, including feed and purge flow rates, adsorption and desorption step times, and the number of cycles, are detailed in Table 6.5.

Figures 6.13 and 6.14 display the cyclic steady state (CSS) of a simplified 2-step PSA experiment (performed at 423 K and 473 K, respectively), i.e., (i) pressurization and adsorption

with feed and (ii) vacuum countercurrent depressurization with inert He purge (desorption). Both experiments revealed that at step I (adsorption), the mass front of the HRON 22DMB and iC5 has completely left the column, while the mass transfer front of 23DMB is concentrated at the edge of the column. The other LRON molecules mostly remain inside the bed, with only a small concentration leaving the column at the end of the adsorption step I. Moreover, the CSS was quickly attained for the given experimental conditions, being reached after five cycles at 423 K and nine cycles at 473 K. The real-time RON history shows that the product mixture has an average RON higher than 93 for both temperatures. The evolution of the concentration profiles of HRON and LRON molecules during the continuous cyclic operation until reaching the CSS and the corresponding pressure history of each cycle are shown in Figures D.1 – D.4 of *Appendix D*.

Table 6.5 | Experimental conditions for the preliminary 2-step PSA experiments with an equimolar septenary mixture of pentane and hexane isomers in a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A.

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol}.\text{min}^{-1}$)	He flow rate (feed) ($\text{mL}.\text{min}^{-1}$)	He flow rate (purge) ($\text{mL}.\text{min}^{-1}$)	Cycles number	Adsorption step time (min)	Desorption step time (min)	Total Duration (min)
7_1	423	50.0	563	12.8	76.7	6	33	18	306
7_2	473	50.0	503	11.4	68.6	10	24	12	360

The mass of MIL-160(Al) and zeolite 5A used in the mixed-bed experiments was 12.8 g and 5.49 g, respectively, packed in column 3 (see Chapter 3);

The flow rates are expressed at STP conditions.

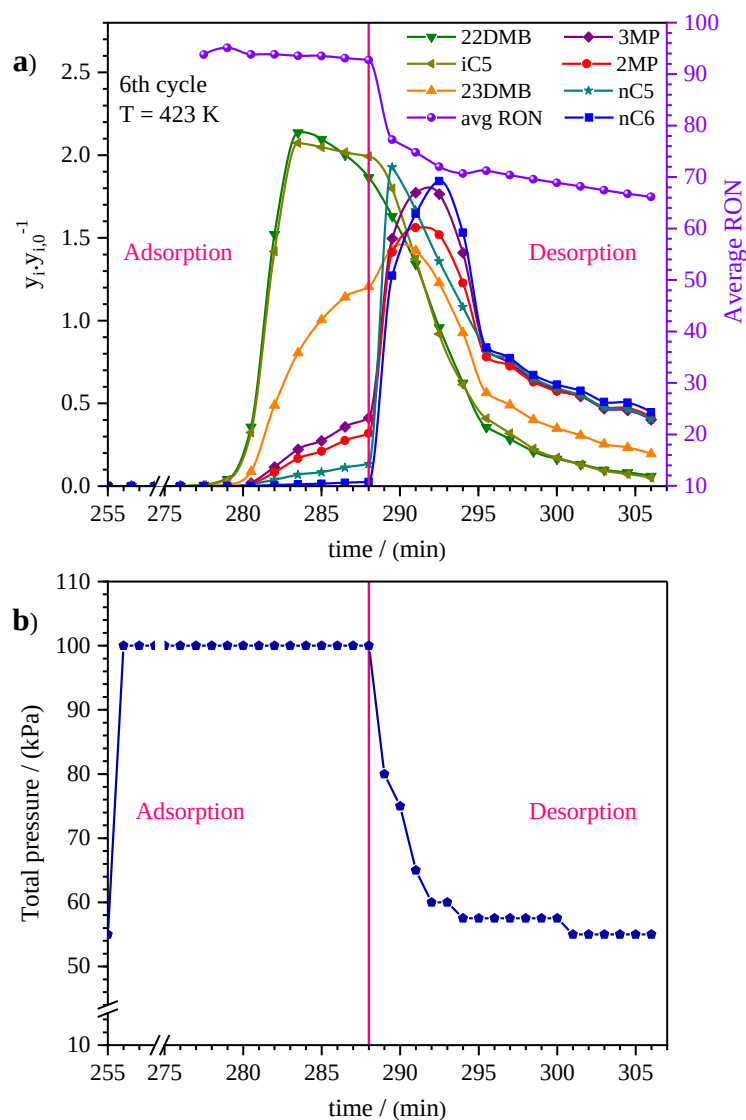


Figure 6.13 | CSS of a simplified PSA experiment for a septenary equimolar mixture of pentane and hexane isomers in a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 423 K and 50 kPa: a) Normalized molar fraction profiles, b) Total pressure history. Adsorption, step I - pressurization and feed; desorption, step II – vacuum countercurrent depressurization followed by inert He purge.

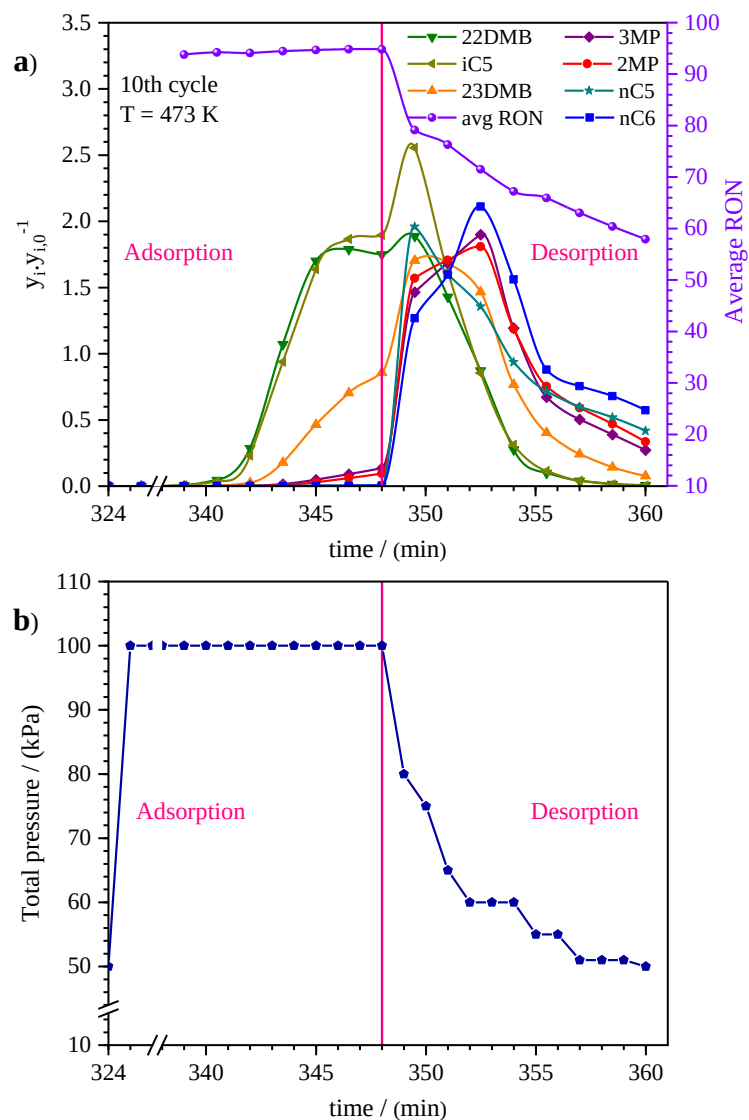


Figure 6.14 | CSS of a simplified PSA experiment for a septenary equimolar mixture of pentane and hexane isomers in a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 473 K and 50 kPa: a) Normalized molar fraction profiles, b) Total pressure history. Adsorption, step I - pressurization and feed; desorption, step II – vacuum countercurrent depressurization followed by inert He purge.

Decisively, these preliminary experiments undoubtedly prove the viability of the novel mixed-bed adsorbent to separate all pentane and hexane isomers in continuous cyclic operation into distinct HRON and LRON fractions. However, this study was not further exploited because it is very difficult to analyse the effluent from the experimental unity conveniently. The high flow rates and pressure changes strongly complicate the calibrations of the chromatographic sample analysis system, and it was not possible in due time to overcome these difficulties. Further money investments should be applied in the future to improve the analytical system of the PSA studies in non-permanent gases. Also, to minimize errors in cyclic operation, the size of the column should be increased to a semi-pilot level to get reliable data, and that should be

performed in an industrial plant of a company interested in this subject. Contacts are being established to transfer this technology to semi-pilot industrial tests.

6.3.3 Modelling Adsorption Equilibrium Isotherms

The fitting results for the single component isotherms of pentane and hexane isomers in MIL-160(Al) have already been shown in Figures 6.7 and 6.8 by the continuous lines, respectively. As demonstrated, model predictions and experimental data are in fairly agreement. For the fitting procedure, the loadings obtained from the single (Table 6.3) and multicomponent (Table 6.4) breakthrough experiments were correlated with the DSL isotherm model described in *Chapter 3*, which distinguishes two categories of sorption sites, A and B, each one following a Langmuir behaviour.

There are at least 56 parameters to be determined for the seven pure gas adsorption equilibrium isotherms. Therefore, to simplify the fitting procedure, it was considered that the saturation loading capacity is independent of the adsorbate, i.e., the sum of $q_{max,i}$ of the two sites is equal for all alkane isomers. Moreover, this parameter was also assumed as being temperature-dependent, meaning that the thermal expansion factor of all components (Eq. 3.8, *Chapter 3*) should be equal and the same in both sites ($\delta_A = \delta_B$). These assumptions eliminate some degrees of freedom from the numerical procedure and gives some consistency to the model.

The obtained model parameters, reported in Table 6.6, indicate a sum of $q_{max,i}$ equal to 1.85, 1.50, and 1.23 mol.kg⁻¹ at 373, 423, and 473 K, respectively, with the thermal expansion factor corresponding to 1.53. In addition, it is also shown that the affinity to the adsorbent measured by the values of Henry constants, for the three temperatures, is in line with the sorption hierarchy order observed in the breakthrough experiments: nC6 > 2MP > 3MP > nC5 > 23DMB > iC5 $\approx$ 22DMB.

Regarding the equilibrium loadings corresponding to the adsorption of linear alkanes nC5 and nC6 on zeolite 5A, from the multicomponent experiments in the mixed-bed, they were correlated by the simple Langmuir isotherm model (also described in *Chapter 3*). The fitted parameters are reported in Table 6.7. As input for data fitting, we used the $q_{sat,i}$ determined by Silva et al. (1.50 mol.kg⁻¹), who have studied in detail the adsorption of linear paraffins in a fixed bed of zeolite 5A pellets.^{16,19} Although they considered this parameter constant, we

allowed their temperature dependence to achieve a better fitting. As it can be seen, they slightly decrease from 1.50 to 1.43 mol.kg⁻¹, with an associated thermal expansion factor corresponding to 0.186. Once again, the values of Henry constants are compatible with the observed experimental sorption hierarchy order: nC6 > nC5.

Table 6.6 | DSL isotherm parameters for the sorption of pentane and hexane isomers in MIL-160(Al) and average deviation between model predictions and experimental data.

DSL Parameters	Pentane isomers			Hexane isomers			
	nC5	iC5	nC6	2MP	3MP	23DMB	22DMB
$\delta_A = \delta_B$ (-)	1.53	1.53	1.53	1.53	1.53	1.53	1.53
$-\Delta H_A$ (kJ.mol ⁻¹)	65.6	52.7	72.0	71.0	65.7	77.7	86.1
$-\Delta H_B$ (kJ.mol ⁻¹)	33.4	30.1	37.7	35.7	31.8	17.4	8.68
<i>Temperature: 373 K</i>							
$q_{sat1,A}$ (mol.kg ⁻¹)	0.580	0.611	0.952	0.956	0.556	0.683	0.743
$q_{sat1,B}$ (mol.kg ⁻¹)	1.26	1.23	0.893	0.889	1.29	1.16	1.11
$b_{1,A}$ (kPa ⁻¹)	3.77	0.718	12.5	8.35	4.11	3.00	2.58
$b_{1,B}$ (kPa ⁻¹)	0.126	0.0628	0.240	0.147	0.186	0.0589	0.0219
H_1 (mol.kg ⁻¹ .kPa ⁻¹)	2.35	0.516	12.1	8.12	2.52	2.12	1.92
<i>Temperature: 423 K</i>							
$q_{sat2,A}$ (mol.kg ⁻¹)	0.473	0.498	0.776	0.779	0.453	0.557	0.598
$q_{sat2,B}$ (mol.kg ⁻¹)	1.03	1.01	0.728	0.724	1.05	0.947	0.906
$b_{2,A}$ (kPa ⁻¹)	0.311	0.0965	0.804	0.558	0.337	0.155	0.0975
$b_{2,B}$ (kPa ⁻¹)	0.0353	0.0199	0.0571	0.0378	0.0555	0.0304	0.0157
H_2 (mol.kg ⁻¹ .kPa ⁻¹)	0.183	0.0681	0.665	0.463	0.211	0.115	0.0725
<i>Temperature: 473 K</i>							
$q_{sat3,A}$ (mol.kg ⁻¹)	0.385	0.406	0.632	0.635	0.369	0.454	0.487
$q_{sat3,B}$ (mol.kg ⁻¹)	0.840	0.819	0.593	0.590	0.856	0.771	0.738
$b_{3,A}$ (kPa ⁻¹)	0.0433	0.0198	0.0924	0.0662	0.0468	0.0150	0.00735
$b_{3,B}$ (kPa ⁻¹)	0.0130	0.00808	0.0184	0.0129	0.0214	0.0180	0.0121
H_3 (mol.kg ⁻¹ .kPa ⁻¹)	0.0276	0.0147	0.0694	0.0496	0.0356	0.0207	0.0125
$\Sigma \bar{\Delta}q$	0.00689						

* The reference temperature used was $T_0 = 373$ K.

Table 6.7 | Langmuir isotherm parameters for the sorption of linear alkanes in zeolite 5A and average deviation between model predictions and experimental data.

Langmuir Parameters		Linear Alkanes	
		nC5	nC6
δ	(-)	0.186	0.186
$-\Delta H$	(kJ.mol ⁻¹)	16.4	16.6
<i>Temperature: 373 K</i>			
$q_{sat,1}$	(mol.kg ⁻¹)	1.50	1.50
b_1	(kPa ⁻¹)	0.187	0.403
H_1	(mol.kg ⁻¹ .kPa ⁻¹)	0.280	0.605
<i>Temperature: 423 K</i>			
$q_{sat,2}$	(mol.kg ⁻¹)	1.46	1.46
b_2	(kPa ⁻¹)	0.100	0.214
H_2	(mol.kg ⁻¹ .kPa ⁻¹)	0.146	0.313
<i>Temperature: 473 K</i>			
$q_{sat,3}$	(mol.kg ⁻¹)	1.43	1.43
b_3	(kPa ⁻¹)	0.061	0.130
H_3	(mol.kg ⁻¹ .kPa ⁻¹)	0.0872	0.185

* The reference temperature used was $T_0 = 423$ K.

It should be noted that the fitting of the adsorption equilibrium data in both materials was independently performed, in which the thermal expansion factor of the pentane and hexane isomers does not need to be strictly the same in both materials. Moreover, the above parameters should be read as empirical values valid only for the proper description of the considered adsorption system shown in this work.

6.3.4 Numerical Simulations of Multicomponent Breakthrough Curves

Modelling adsorption equilibrium data is essential to shedding light on the overall dynamics of a fixed bed system for thereafter designing a cyclic adsorption process. The numerical simulations for the multicomponent breakthrough curves of hexane isomers in MIL-160(Al), using the dynamic mathematical model described in *Chapter 3*, have already been shown in Figures 6.9 and 6.10 by the continuous lines.

Since the adsorption and separation of pentane and hexane isomers in MIL-160(Al) is primarily based on thermodynamically equilibrium competition (sharp breakthrough curves and overshoot phenomenon) instead of being diffusion-controlled, the numerical simulations were performed considering weak diffusional limitations (high diffusivities). Thus, equal $k_{LDF,i}$ coefficients (Eq. 3.22, *Chapter 3*) for all alkane isomers were adjusted until achieving a global fitting of the experimental data. The obtained values are around 0.00857 s^{-1} at 423 K and 0.0156 s^{-1} at 473 K. Their temperature dependence, calculated from the Arrhenius expression (Eq. 3.23, *Chapter 3*), gave rise to an ΔE_i of 20 kJ.mol^{-1} . In addition, the heat balance revealed that the system is near isothermal, with a maximum temperature deviation detected in the gas phase at the column outlet being around 7 K (run 4_1).

As can be seen from both figures, the shapes of the breakthrough curves were successfully predicted for most alkane isomers, in which their width of the mass-transfer zone and the overshoots in concentration were qualitatively well described. As a next step, the mathematical model deduced in *Chapter 3* was adapted to further reproduce the experimental data collected in the mixed-bed consisting of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A (Figure 6.12). Accordingly:

1) The fundamental material balances for the sorbate species (Eq. 3.20) and overall system (Eq. 3.21) were adjusted to account for the mass transfer rate term of linear paraffins nC5 and nC6 (fluid phase) to zeolite 5A (solid phase), as follows:

$$\varepsilon_{b\_avg} D_{ax} \frac{\partial}{\partial z} \left(C_T \frac{\partial y_i}{\partial z} \right) = \frac{\partial}{\partial z} (F_T y_i) + \varepsilon_{b\_avg} \frac{\partial}{\partial t} (C_T y_i) + \rho_{b\_mb} \sum_{j=1}^{N_M} x_j \frac{\partial \bar{q}_{i,j}}{\partial t} \quad (6.1)$$

$$\frac{\partial F_T}{\partial z} + \varepsilon_{b\_avg} \frac{\partial C_T}{\partial t} + \rho_{b\_mb} \sum_{j=1}^{N_M} \left(x_j \sum_{i=1}^{N_c} \frac{\partial \bar{q}_{i,j}}{\partial t} \right) = 0 \quad (6.2)$$

where ρ_b (kg.m^{-3}) is the bulk density of the mixed-bed and is calculated using the ratio of the total mass (MIL-160(Al) + zeolite 5A) over the volume of the adsorption column, N_M is the number of adsorbent materials in the bed, and x_j is the fraction of material j packed in the column. The rate $(\partial \bar{q}_{i,j} / \partial t)$ is also expressed by the LDF model approximation (Eq. 3.22).

2) The fundamental energy balance for the solid phase (Eq. 3.25) was adjusted to account for the heat generated corresponding to the adsorption of the linear paraffins in zeolite 5A, as shown

in Eq. 6.3. To simplify, a homogeneous temperature for the solid phase was assumed, in which both materials (MIL-160(Al)/zeolite 5A) contribute for its variation;

$$\rho_{a\_avg} c_{ps\_avg} \frac{\partial T_s}{\partial t} = a_{s\_avg} h_f (T_g - T_s) + \sum_{j=1}^{N_M} \left(\rho_{a,j} \sum_{i=1}^{N_c} (-\Delta H_{i,j}) \frac{\partial \bar{q}_{i,j}}{\partial t} \right) \quad (6.3)$$

3) Solid properties such as ρ_{a_avg} , c_{ps_avg} , a_{s_avg} , d_{p_avg} , and k_{s_avg} , were weighted averaged. The porosity of the packed bed, ε_{b_avg} , is calculated using ρ_{b_mb} and ρ_{a_avg} . These averaged properties were used in the whole set of equations of the numerical package.

Therefore, the fitted parameters for MIL-160(Al) (DSL, Table 6.6) and zeolite 5A (Langmuir, Table 6.7) were inserted in the dynamic mathematical model with the adapted material and energy balances to perform the breakthrough simulations on the mixed-bed. Similar to MIL-160(Al), the $k_{LDF,i}$ coefficients for the adsorption of nC5 and nC6 in zeolite 5A were obtained by matching the experimental data. The estimated values for both paraffins are around 0.00354 s^{-1} at 423 K and 0.00556 s^{-1} at 473 K, which gave rise to a corresponding ΔE_i of 15 kJ.mol^{-1} . The system continues to be near isothermal.

The numerical results from Figure 6.12 show once more that the breakthrough curves were well described, from where the dynamic model captured the change in the adsorption behaviour of nC5, leaving the column after the mono-branched hexanes. Besides, it reproduces the desired discrimination between fractions of HRON (22DMB, 23DMB, and iC5) and LRON (nC6, nC5, 2MP, and 3MP) alkanes. Minor deviations were found at 423 K (Figure 6.12a) in the shapes of 3MP, 2MP and nC6 hexanes, where the simulated breakthroughs are slightly steeper.

Globally, the simulation results from single and mixed-bed adsorption showed satisfactory agreement with the experimental data. We believe that is mainly due to the accurate description of the adsorption equilibrium of pentane and hexane isomers in MIL-160(Al) by the DLS isotherm model. These observations open a good perspective for future work, in which the mixed-bed model will be upgraded for simulating a cyclic adsorption operation in order to optimise the working conditions, such as cycle time, purge-to-feed ratio, and the mixed-bed ratio of MOF/Zeolite. As MIL-160(Al) can easily be scaled-up under ambient pressure green conditions, this paves the way for future pilot-scale tests based on the numerical predictions from the dynamic mathematical model.

All the model parameters used for the numerical simulations of the breakthrough curves in a single (MIL-160(Al)) and mixed-bed (MIL-160(Al)/zeolite 5A) adsorption are summarised in Tables D.1 – D.3 of *Appendix D*.

6.4 Conclusions

This chapter reveals that a synergistic action of a mixed-bed made by the robust bio-derived MOF MIL-160(Al) together with the benchmark zeolite 5A achieves an efficient thermodynamic / size exclusion separation of pentane and hexane isomers into valuable HRON (22DMB, iC5, and 23DMB) and LRON (nC6, nC5, 2MP and 3MP) fractions. This synergistic action is required to prevent the elution of the LRON nC5 together with 23DMB in the HRON fraction if only a single bed of MOF MIL-160(Al) is used. As a result, it was demonstrated that a spectacular separation under relevant industrial working conditions is achieved with an exceptional 92 RON ideal productivity of 1.14 mol.dm⁻³.

Through preliminary PSA experiments, this MOF/zeolite duo mixed-bed was proven to work under cyclic operation and therefore be incorporated in the TIP process. As MIL-160(Al) can be produced at multi-kilogram scale with a predicted low-cost industrial production while zeolite 5A is already commercially available, this gives the building block for further testing at pilot scale prior to envisaging industrial commercialization. In addition, the calibrated dynamic mathematical model can be used for respective optimization of working conditions. This advanced staged recycling technology might not only provide the production of higher quality clean gasoline but also fills the gap in the current industrial adsorption separation science by combining two prominent classes of porous materials, paving the way for the design of new separative processes that will exploit MOFs and zeolites complementary features.

6.5 References

- (1) Brântuas, P. F.; Henrique, A.; Wahiduzzaman, M.; Von Wedelstedt, A.; Maity, T.; Rodrigues, A.; Nouar, F.; Lee, U.-H.; Cho, K. H.; Maurin, G.; Silva, J. A. C.; Serre, C. Separation of Branched Alkane Feeds by a Synergistic Action of Zeolite and Metal-Organic Framework. *Adv. Sci.* **2022**, 2201494.

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- (2) Cadiau, A.; Lee, J. S.; Damasceno Borges, D.; Fabry, P.; Devic, T.; Wharmby, M. T.; Martineau, C.; Foucher, D.; Taulelle, F.; Jun, C. H.; Hwang, Y. K.; Stock, N.; De Lange, M. F.; Kapteijn, F.; Gascon, J.; Maurin, G.; Chang, J. S.; Serre, C. Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation. *Adv. Mater.* **2015**, *27*, 4775–4780.
- (3) Permyakova, A.; Skrylnyk, O.; Courbon, E.; Affram, M.; Wang, S.; Lee, U. H.; Valekar, A. H.; Nouar, F.; Mouchaham, G.; Devic, T.; De Weireld, G.; Chang, J. S.; Steunou, N.; Frère, M.; Serre, C. Synthesis Optimization, Shaping, and Heat Reallocation Evaluation of the Hydrophilic Metal–Organic Framework MIL-160(Al). *ChemSusChem* **2017**, *10*, 1419–1426.
- (4) Permyakova, A.; Wang, S.; Courbon, E.; Nouar, F.; Heymans, N.; D’Ans, P.; Barrier, N.; Billefont, P.; De Weireld, G.; Steunou, N.; Frère, M.; Serre, C. Design of Salt-Metal Organic Framework Composites for Seasonal Heat Storage Applications. *J. Mater. Chem. A* **2017**, *5*, 12889–12898.
- (5) Damasceno Borges, D.; Normand, P.; Permyakova, A.; Babarao, R.; Heymans, N.; Galvao, D. S.; Serre, C.; De Weireld, G.; Maurin, G. Gas Adsorption and Separation by the Al-Based Metal-Organic Framework MIL-160. *J. Phys. Chem. C* **2017**, *121*, 26822–26832.
- (6) Wu, X.; Wei, W.; Jiang, J.; Caro, J.; Huang, A. High-Flux High-Selectivity Metal–Organic Framework MIL-160 Membrane for Xylene Isomer Separation by Pervaporation. *Angew. Chemie - Int. Ed.* **2018**, *57*, 15354–15358.
- (7) Brandt, P.; Nuhnen, A.; Lange, M.; Möllmer, J.; Weingart, O.; Janiak, C. Metal-Organic Frameworks with Potential Application for SO₂ Separation and Flue Gas Desulfurization. *ACS Appl. Mater. Interfaces* **2019**, *11*, 17350–17358.
- (8) Gordeeva, L. G.; Solovyeva, M. V.; Sapienza, A.; Aristov, Y. I. Potable Water Extraction from the Atmosphere: Potential of MOFs. *Renew. Energy* **2020**, *148*, 72–80.
- (9) Reinsch, H.; Van Der Veen, M. A.; Gil, B.; Marszalek, B.; Verbiest, T.; De Vos, D.; Stock, N. Structures, Sorption Characteristics, and Nonlinear Optical Properties of a New Series of Highly Stable Aluminum MOFs. *Chem. Mater.* **2013**, *25*, 17–26.
-

- (10) Triebl, C.; Nikolakis, V.; Ierapetritou, M. Simulation and Economic Analysis of 5-Hydroxymethylfurfural Conversion to 2,5-Furandicarboxylic Acid. *Comput. Chem. Eng.* **2013**, *52*, 26–34.
- (11) BASF. Synvina: Joint Venture of BASF and Avantium established <https://www.basf.com/global/en/media/news-releases/2016/10/p-16-322.html>.
- (12) Severino, M. I.; Gkaniatsou, E.; Nouar, F.; Pinto, M. L.; Serre, C. MOFs Industrialization: A Complete Assessment of Production Costs. *Faraday Discuss.* **2021**, *231*, 326–341.
- (13) Jänchen, J.; Schumann, K.; Thrun, E.; Brandt, A.; Unger, B.; Hellwig, U. Preparation, Hydrothermal Stability and Thermal Adsorption Storage Properties of Binderless Zeolite Beads. *Int. J. Low-Carbon Technol.* **2012**, *7*, 275–279.
- (14) Belviso, C. *Zeolites - Useful Minerals*; IntechOpen, 2016.
- (15) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069.
- (16) Silva, J. A. C.; Rodrigues, A. E. Equilibrium and Kinetics of N-Hexane Sorption in Pellets of 5A Zeolite. *AIChE J.* **1997**, *43*, 2524–2534.
- (17) Ivan Moraes Costa Pinto. Adsorption of Pentane/Hexane Isomers in Metal Organic Frameworks. Master's Thesis, Instituto Politécnico de Bragança - Escola Superior de Tecnologia e de Gestão, 2020.
- (18) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels. *Science*. **2013**, *340*, 960–964.
- (19) Silva, J. A. C.; Rodriguez, A. E. Sorption and Diffusion of N-Pentane in Pellets of 5A Zeolite. *Ind. Eng. Chem. Res.* **1997**, *36*, 493–500.

7 SEPARATION OF N/ISO-PARAFFINS IN A HIERARCHICALLY STRUCTURED 3D-PRINTED POROUS CARBON MONOLITH

The content of this chapter is based on:

Henrique, A.; Steldinger, H.; Diaz de Tuesta, J. L.; Gläsel, J.; Rodrigues, A. E.; Gomes, H. T.; Etzold, B. J. M.; Silva, J. A. C. Separation of n/iso-Paraffins in a Hierarchically Structured 3D-Printed Porous Carbon Monolith. To be submitted

A series of hierarchically structured 3D-printed porous carbons monoliths, exhibiting cylinder structures composed of tetragonal cubic centred unit cells, were investigated regarding their ability to separate pentane and hexane isomers feed mixtures. Three materials differentiating by their degree of CO₂ activation were evaluated: non-activated and activated at 1133 K for 6 and 12 h, respectively. Multicomponent experiments with equimolar septenary mixtures were performed, covering the temperatures of 373, 423, and 473 K and total alkane pressure up to 50.0 kPa. Results demonstrated that the non-activated monolith enables the complete separation of linear paraffins from their respective branched isomers (slightly adsorbed) via a near molecular sieving effect, showing the following sorption hierarchy order nC6 > nC5 >>> 2MP > 3MP > 23DMB $\approx$ iC5 > 22DMB. The Langmuir isotherm conveniently fitted the adsorption equilibrium, being the simulated breakthrough curves suitably predicted by the dynamic mathematical model. From the fitting of the experimental breakthrough curves, equal k_{LDF} coefficients for the linear paraffins were used in the simulations, ranging from 0.00180 – 0.00310 s⁻¹. Concerning the CO₂ activated monoliths, both showed a completely different picture, in which the near molecular sieving separation of n/iso-paraffins disappeared with the adsorption of all alkane isomers. The elution order has also changed, with the pentane isomers eluting first from the column, then followed by the hexane isomers: nC6 > 3MP > 2MP > 23DMB > 22DMB > nC5 > iC5. These results indicate that besides enhancing the microporosity of the monoliths, there is also pore widening during the CO₂ activation process. Consequently, much higher loadings were achieved, at least three times higher than those on the non-activated monolith.

7.1 Introduction

Structuring adsorbent materials that could be easily implemented in large-scale processes is a fundamental step in their way towards commercialization. Porous materials synthesized by different reactions (solvothermal/hydrothermal) are mostly generated as fine particles in the powdered state, which must be transformed into well-shaped bodies prior to industrial use while preserving the intrinsic properties of the powder. Otherwise, the particulate scatters and contaminates the engineering facility. Techniques for producing appropriate macro-structured geometric forms, namely granules, pellets, and beads or extrudates, have been widely developed as a route for powder scale-up.¹⁻¹⁰ However, the frequent problems associated with the use of these shaped materials in packed bed systems when higher throughputs are required, such as the considerable pressure drop at high gas velocities, mass transfer restrictions related to gas diffusion into or out of the materials, and low mechanical/attrition resistance impose limitations in operating such processes at optimum conditions in terms of energy consumption and overall system efficiency.^{11,12}

Motivated by that, there has been a significant effort to devise new strategies to yield structured adsorbents into other configurations that could overcome these issues of traditional packing systems. In this regard, the monolithic engineered geometry has gained a great deal of attention as an alternative way to manufacture adsorbent materials.¹³ Monolithic contactors present a unique geometry configuration consisting of parallel channels (i.e., continuous body with identical channels), which do not impart resistance to fluid flow. Therefore, resulting in a uniform flow pattern associated with a lower pressure drop across the bed while offering enhanced mass and heat transfer characteristics.^{11,12} Such well-designed robust contactors are structured materials in which the shape and the diameter of the parallel channels, the wall thickness, and their cell density are controllable.¹⁴

Conventionally, these geometrically patterned materials have been manufactured using the extrusion technique, where the adsorbent is adhered to a putty, pressed through a mould, and fired to harden the final structure.¹⁵ However, this method is costly and limited in offering flexibility to design complex structures with tailored geometry since the extrudate mould must be tailor-made for each column geometry.^{16,17} Besides, this technique does not apply to mostly MOFs since the firing step burns out the organic linker and decomposes the crystallite.¹⁵ On the other hand, 3D printing technology, also known as rapid prototyping or additive manufacturing, has raised considerable interest over the past few years since this technique

allows for the digital design of the material structure, circumventing the need to manufacture extrudate molds.¹⁵ More specifically, the material geometry is modelled in a 3D computer-aided design (CAD) software attached to 3D printers. Then, the software generates a special type of file (Standard Tessellation Language - STL) to be sent to the printer, which reads the file and generates the material by adjoining one layer over the other.^{15,18} The unique design flexibility associated with the diversity of printing methods characterizes 3D printing as a more efficient and powerful technology for fabricating structured materials than traditional extrusion processes.

Currently, most publications dealing with the application of 3D-printed monoliths as adsorbents are in the field of CO₂ capture from the air/enclosed environments or post-combustion flue gas. Structures made of different material classes, such as aminosilica¹⁹ (PEI-, TEPA-, APS-silica), zeolites^{14,20,21} (5A, 13X, SAPO-34, and ZSM-5), polymer-zeolites²² (Torlon-zeolite 13X and Torlon-zeolite 5A), MOFs^{16,23-26} (MOF-74(Ni), UTSA-16, and amine-functionalized MIL-101), polymer-MOFs²⁷ (40HKUST-1@Torlon and MOF-74@Torlon), and activated carbons¹⁷ have been reported. In addition, hybrid 3D-printed zeolitic/carbonaceous monolith structures (zeolite 13X/AC and zeolite 13X/graphite) have been also developed.^{28,29} These works show the heterogeneity in adsorbent materials that can be utilized using the 3D printing technique. Interesting outcomes were obtained, with most monolithic adsorbents displaying comparable CO₂ uptake and separation performance, fast adsorption kinetics, relative stability, and regenerability to their powder analogues. Moreover, the hybrid monoliths showed electrical conductivity properties (measured through their heating by the Joule effect) that postulate them as a promising option for CO₂ capture by Electrical Swing Adsorption (ESA) processes.

So far, to the best of our knowledge, there is no literature data on the use of monolithic adsorbents for the separation of alkane isomers. However, Steldinger et al.³⁰ have recently developed a novel flexible, fast, and reproducible printing technique for obtaining hierarchically structured porous carbons with high final carbon yield and controlled porosity, which holds promise for identifying optimal carbonaceous structures that can be applied to multiple fields in adsorption separation processes. The method is built on stereographically (SLA) 3D printing of a porous polymer, which is then transformed into activated carbon by a thermal treatment. By implementing a porogen templating into the printing process, meso- and macropores were successfully introduced in the polymer precursor. Thereafter, in an optimized oxidation and pyrolysis procedure, an additional fraction of micropores was introduced in the

material, while the macrostructure and templated pores were retained. Additional CO₂ activation enabled a high surface area to the 3D-printed monolith, in which an increase from 536 m².g⁻¹ for non-activated carbon to 2200 m².g⁻¹ for the activated at 1173 K was achieved. Mechanical stability was maintained throughout the process.

This being stated, we aimed to evaluate the potential applicability of these recently discovered porous carbons structures in the third dimension to separate pentane and hexane isomers mixtures. The first section of this chapter, Section 7.2, fully describes the 3D printing methodology applied to manufacture three monolithic adsorbents with the same open cell structures but subject to different degrees of CO₂ activation. In addition, the material's porosity is evaluated by N₂ sorption isotherms. In Section 7.3, the experimental and numerical results are shown. A series of experimental breakthrough curves with septenary mixtures of all pentane and hexane isomers are performed exploiting the effect of the temperature and total alkane pressure. Initially, a direct comparison of the breakthrough data for each 3D-printed monolith is given under the same working conditions to clarify their separation performance based on the degree of CO₂ activation. Then, the equilibrium data for the non-activated monolith is modelled by the Langmuir isotherm and fitted parameters used in the dynamic mathematical model for the numerical simulations. As a final point, a summary of the key findings of the chapter is given in Section 7.4.

7.2 3D-Printed Monoliths: Synthesis and Characterization

The synthesis of the hierarchically structured 3D-printed monoliths was carried out at *Etzoldlab* of the *Technische Universität Darmstadt (TU Darmstadt)*, and their characterization at *Microtrac Retsch GmbH*. The data is detailed below.

7.2.1 Synthesis of 3D-Printed Monoliths

The materials were prepared following a procedure recently developed by Steldinger,³¹ as demonstrated in Figure 7.1. Accordingly, it consists of 4 main steps: i) resin preparation; ii) photopolymerization; iii) porogen extraction, and iv) thermal treatment.

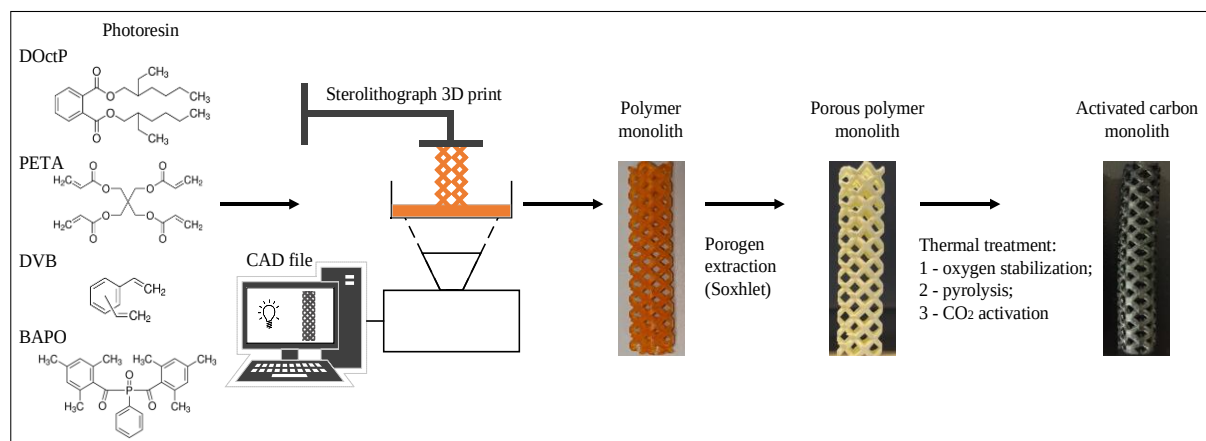


Figure 7.1 | Schematic illustration of the 3D printing process. Initially, the liquid resin is prepared; after that, a porous polymer open cell structure is generated by photopolymerization (stereolithographic 3D print), which is followed by the extraction of the non-reactive porogen phase; and then an activated carbon open cell structure is obtained upon a thermal treatment consisting of stabilization in air, pyrolysis in nitrogen and activation in CO₂. Adapted from the ref. 31

i) Resin preparation: the resin mixture prepared for stereolithography was formulated with two monomers as major components (70%), an inert porogen (30%), which should not participate in photopolymerization, but result in phase separation (low solubility) and pore template formation, an initiator to start the polymerization at illuminated spots, and a dye to control light penetration depth. In a typical 3D printing process, 100 mL of the resin were prepared with the following reagents: 35 mL of pentaerythritol tetraacrylate (PETA, containing 10 – 40% triacrylate, 350 ppm hydroquinone) and 35 mL of divinylbenzene (DVB, containing 20% ethylstyrene, 1000 ppm p-tert-butylcatechol) as monomers; 30 mL of bis(2-ethylhexyl) phthalate (DOctP, $\geq 98\%$) as porogen; 0.4 mg.mL⁻¹ of colour agent sudan1 ($\geq 95\%$), and 10 mg.mL⁻¹ of phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO, 97%) as initiator. All the reagents are from *Sigma Aldrich*, except the porogen DOctP purchased from *Alfa Aesar*. Initially, the three liquid components, PETA, DVB, and the porogen, were mixed in a Schott bottle. Thereafter, the colour agent sudan1 and the initiator BAPO were added to the mixture. Then the prepared mixture was placed in an orbital shaker at 350 rpm until achieving a homogeneous state. The Schott bottle was enwrapped with aluminium foil to avoid starting the photopolymerization prematurely;

ii) Photopolymerization: for the 3D printing, a digital light processing (DLP) based stereolithography printer (*Titan 2 HR, Kudo 3D*) was used. The set-up was adjusted by introducing a blue light filter (Schott BG-3) between the DLP projector and the resin vat. The custom-made resin vat consisted of an aluminium frame with outer dimensions of 180 (width) x 220 (length) x 30 mm (height), leaving an inner space of 140 x 180 mm. A 125 μ m thick

fluorinated ethylene propylene (FEP) film was fixed on this frame with adhesive tape. The 3D printing process consists of the sequential illumination to photopolymerize single layers, with the elevation of the build platform to detach the printed part from the resin vat. First, a single layer height of 4 mm was printed by illuminating the photoresin with a 30×0.5 mm rectangle image for 240 s, applying a lifting speed of $2 \text{ mm} \cdot \text{min}^{-1}$ and lowering speed of $10 \text{ mm} \cdot \text{s}^{-1}$. Subsequently, a lift height of 2 mm, illumination time of 75 s, lifting speed of $4 \text{ mm} \cdot \text{min}^{-1}$, and lowering speed of $50 \text{ mm} \cdot \text{s}^{-1}$ were employed for producing the open-cell structures;

iii) Porogen extraction: after the 3D printing, the polymer structure generated is operated in a Soxhlet extractor (100 mL, without thimble) to remove the porogen DOctP and the colour agent Sudan1. The extraction is processed at 373 K for 24 h, using acetone as solvent ($> 20 \text{ mL} \cdot \text{g}_{\text{polymer}}^{-1}$). Afterwards, the polymer was dried at 333 K overnight in an oven;

iv) Thermal treatment: the last step consists of the thermal treatment of the extracted polymer structures at different temperatures and atmospheres in a tubular quartz glass furnace (*Carbolite Gero*). Before each thermal treatment, the tubular furnace was evacuated with a vacuum pump and refilled with nitrogen to atmospheric pressure (101.3 kPa). Initially, the 3D-printed polymer was oxidized in the air ($30 \text{ NL} \cdot \text{h}^{-1}$) for 6 h at 573 K. A heating ramp of $10 \text{ K} \cdot \text{min}^{-1}$ using nitrogen ($10 \text{ NL} \cdot \text{h}^{-1}$) was applied until reaching the set-point temperature. Thereafter, the oxidized sample is pyrolyzed under a nitrogen atmosphere ($10 \text{ NL} \cdot \text{h}^{-1}$) at 1173 K for 0.3 h. For that, a heating ramp of $3.3 \text{ K} \cdot \text{min}^{-1}$ is used. Finally, CO_2 activation was applied to increase the microporosity of the resulting carbonaceous structure. The same heating ramp with nitrogen used for the oxygen stabilization step was applied in this stage.

The digital design of the monolith was performed in the programming-based compiler OpenSCAD, a free software for creating solid 3D CAD objects (the source code can be found elsewhere³¹). The material comprises 8 tetragonal cubic centred unit cells (Figure 7.2a), with a unit cell diameter of 5.7 mm and a thread diameter of 2 mm. The 3D model design was then exported in STL file format and processed with a slicing program, the JavaScript application *SLAcer*. The slicing process yielded a zip file containing a numbered of single images (png-file) corresponding to each slice, which was uploaded to the 3D printing software and thus used for the printing. For this study, three monoliths with different degrees of CO_2 activation were prepared: 1) non-activated (M1), 2) activated at 1133 K for 6 h (M2), and 3) activated at 1133 K for 12 h (M3) (Figure 7.2b).

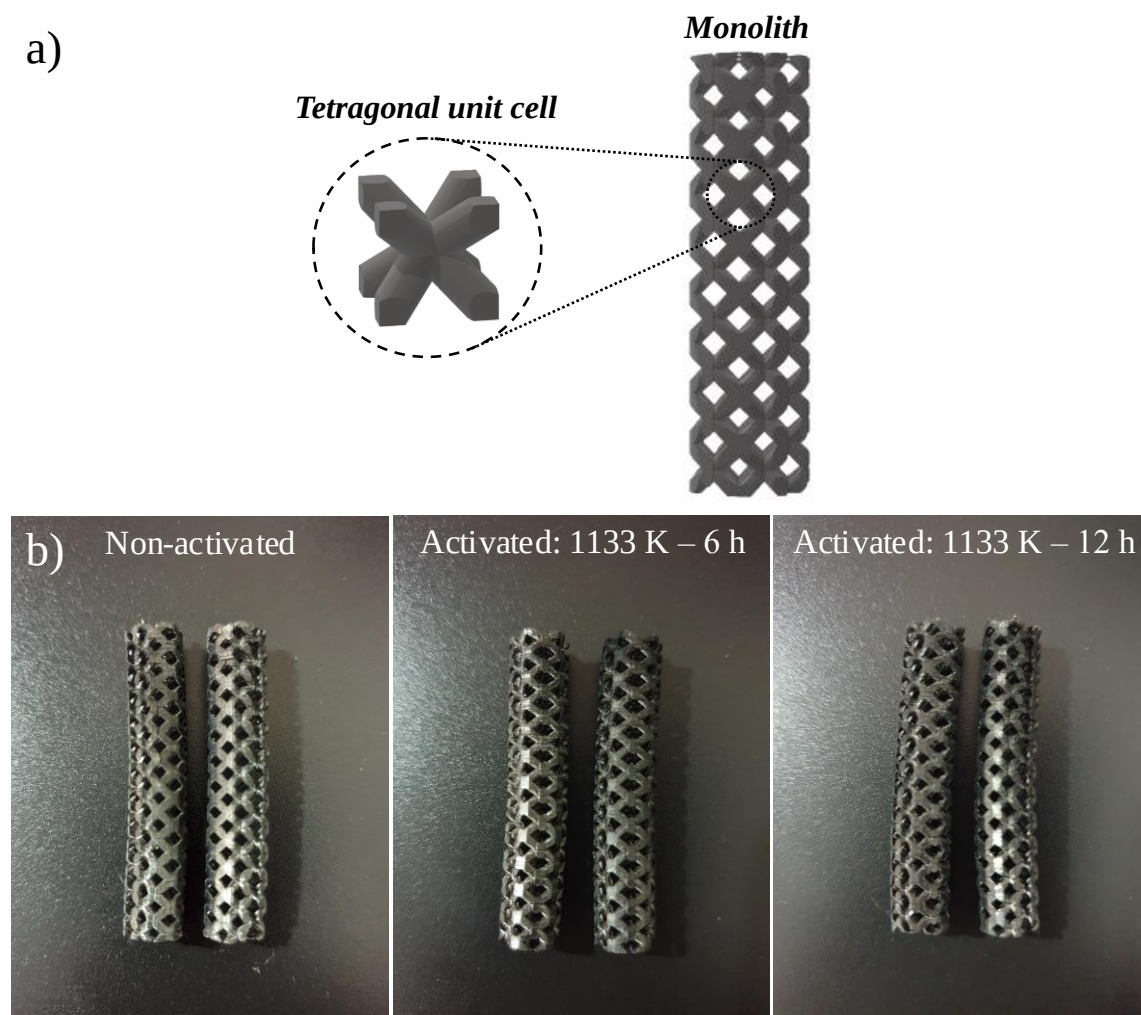


Figure 7.2 | Schematic view of 3D-printed monoliths: a) CAD structure used for the stereolithographic 3D printing, and b) Photo records of materials' final forms.

7.2.2 N₂ Adsorption and Desorption Isotherms of 3D-Printed Monoliths

Gas sorption measurements were conducted to give insight into the porosity of the 3D-printed monoliths. N₂ adsorption and desorption isotherms of the activated monoliths M2 and M3 were measured in a surface area analyser (*BELSORP MAX II, Microtrac Retsch GmbH*), at a temperature of 77 K and a pressure range of $2 \cdot 10^{-6}$ – $1 \cdot 10^2$ kPa. Beforehand, the samples ($\approx$ 90 mg) were degassed at 523 K for 4 h under fine vacuum. The results from the N₂ sorption characterization are presented in Figure 7.3. The data for the monolith M1, also shown in the figure, were taken from the work previously reported by Steldinger et al.³⁰

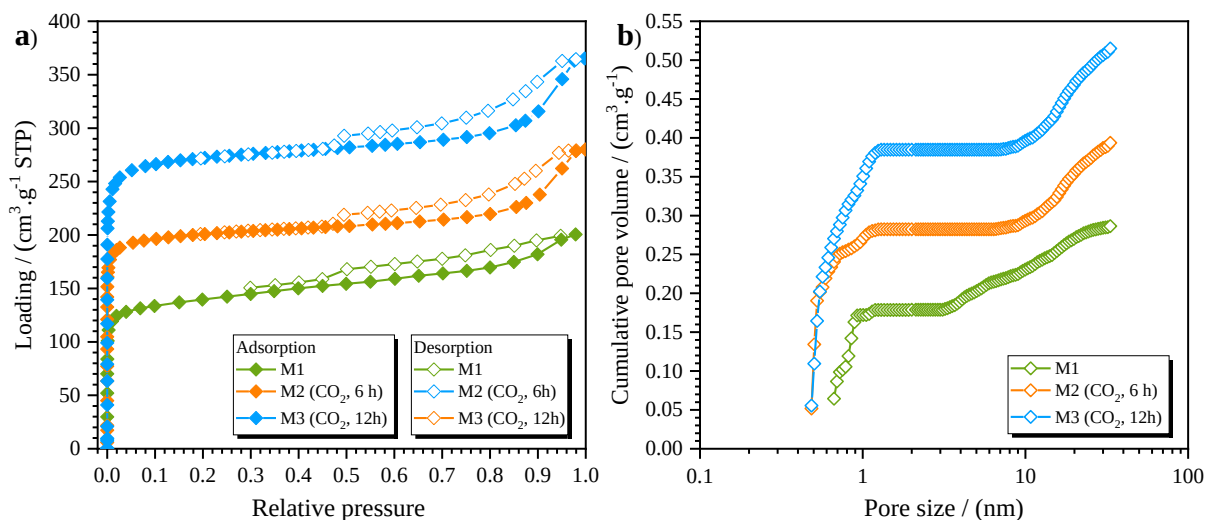


Figure 7.3 | N₂ sorption measurements at 77 K of 3D-printed monoliths: a) Adsorption and desorption isotherms and **b)** Cumulative pore volume distribution.

As it can be seen, the N₂ isotherms (Figure 7.3a) for the three monoliths show a combination of type I and IV, according to the updated IUPAC classification, pointing out the combined micro- and mesoporous character of these materials.³² For microporous solids, the type I isotherm shows an almost vertical branch in the first region of the curve, which is related to enhanced adsorbent-adsorptive interactions in narrow pores, resulting in micropore filling. Indeed, the figure reveals that at very low relative pressures (p/p_0 between $2 \cdot 10^{-8}$ to $5 \cdot 10^{-2}$), the N₂ adsorption progressively increases to around 130, 190, and 260 cm³.g⁻¹ for the monoliths M1, M2, and M3, respectively. On the other hand, at higher relative pressures, hysteresis loops, which are generally associated with capillary condensation, are also visible for the three materials, being this phenomenon characteristic of type IV isotherms given by mesoporous solids. Based on their shapes, the hysteresis loops can be classified as H4, often found in micro-mesoporous carbons, and show a characteristic step down at relative pressure of around 0.45.

As explained above, the macroscopic size and shape of the monoliths are determined by the computer-designed structure, while on the nm level, the porosity can be varied via the CO₂ activation conditions. By increasing the activation time at a temperature of 1133 K from 6 to 12 h, the burn-off almost linearly scales from 13.6 to 26.3 wt.%. The partial oxidation of monoliths M2 and M3 led to a distinct rise of the N₂ uptake in the low-pressure region of the adsorption branch ($p/p_0 < 5 \cdot 10^{-2}$) compared to M1, indicating the creation of additional microporosity due to the materials burn-off and to the opening of pores that could not be accessed priorly.

The physical and textural properties of the monoliths, determined from the N₂ sorption measurements, are summarised in Table 7.1. The specific surface area was calculated applying the BET multi-point method considering five appropriate data points (S_{BET}), and the Quenched solid density functional theory for carbon with a combined slit- and cylindrical pore geometry (S_{QSDFT}). In addition, pore size distributions and the total pore volume were also deduced by the QSDFT model (fitting errors < 0.2%, *VersaWin Vers. 1.0*).

The prolonged activation time equally increases the specific surface area and pore volume of the monolith M3 (S_{QSDFT} : 1307 m².g⁻¹; 0.52 cm³.g⁻¹) compared to M2 (S_{QSDFT} : 1048 m².g⁻¹; 0.39 cm³.g⁻¹). Moreover, according to the cumulative pore volume distributions shown in Figure 7.3b, the largest gain in monoliths M2 and M3 can be attributed to micropores with a diameter less than 1.5 nm. This means that the CO₂ activation process can be utilized as a viable tool to introduce additional micropores without excessive altering the mesoporosity. Apart from this, it should be mentioned that both activated monoliths were stable and could be normally handled in the laboratory.

Table 7.1 | Physical and textural properties of 3D-printed monoliths determined by N₂ sorption measurements.

Physical properties				
		M1*	M2*	M3*
Burn-off	(%)	-	13.6	26.3
Total mass (dry)	(g)	2.36	1.94	1.66
Total length	(mm)	84.0	84.0	84.0
Diameter	(mm)	8.00	8.00	8.00
N ₂ sorption data				
S_{BET}	(m ² .g ⁻¹)	538	805	1078
S_{QSDFT}	(m ² .g ⁻¹)	536	1048	1307
Total pore volume	(cm ³ .g ⁻¹)	0.286	0.394	0.515

* Each monolith consists of two individual pieces resulting in the respective total mass and length.

7.3 Results and Discussion

7.3.1 Multicomponent Adsorption of Pentane and Hexane Isomers in 3D-Printed Monoliths

The adsorption behaviour of pentane and hexane isomers on the hierarchically structured 3D-printed porous carbons monoliths were evaluated through a series of multicomponent breakthrough experiments. Equimolar septenary mixtures with all the alkane isomers (nC5/iC5/nC6/2MP/3MP/23DMB/22DMB) were measured at three different temperatures, 373, 423, and 473 K, and with total alkane pressure up to 50.0 kPa. The carrier gas He was used to set a total pressure in the column of 101.3 kPa. Complete information on the experimental conditions for the fixed bed runs, which were determined in order to ensure a gas residence time in the bed of around 20 s, are given in Table 7.2. The calculated equilibrium loadings for each alkane specie and the corresponding mixture loadings for each run performed are also reported in the table. An overall analysis of these data revealed that, for the three monoliths, the loadings increase as the total alkane pressure increase (at a constant temperature) and decrease as the temperature increase (at a constant total alkane pressure), therefore being thermodynamically consistent.

Figure 7.4 shows the breakthrough curves for the temperature of 373 K and total alkane pressure of 50.0 kPa. The 3D-printed monoliths are expressed in the panels: a) M1, b) M2, and c) M3. For a direct comparison, the ratio of the normalized molar fraction of each alkane is plotted as a function of the total moles of paraffins fed to the column per unit mass of adsorbent (see Eq. 4.1, *Chapter 4*).

Table 7.2 | Experimental conditions for measuring breakthrough curves for an equimolar septenary mixture of pentane and hexane isomers in 3D-printed monoliths and results.

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol.min}^{-1}$)	He flow rate (mL.min^{-1})	q_i (mol.kg^{-1})							q_{mix} (mol.kg^{-1})	S_s
					iC5	nC5	22DMB	23DMB	3MP	2MP	nC6		
<i>Monolith M1 (non-activated)</i>													
1_1	373	10.0	20.4	4.17	0.0186	0.187	0.0125	0.0227	0.0448	0.0618	0.412	0.759	3.73
1_2	373	25.0	51.0	3.48	0.0208	0.202	0.0145	0.0241	0.0488	0.0691	0.433	0.812	3.58
1_3	373	50.0	102	2.32	0.0261	0.209	0.0206	0.0294	0.0523	0.0722	0.445	0.855	3.26
1_4	423	10.0	18.0	3.68	0.0176	0.152	0.00846	0.0199	0.0378	0.0550	0.342	0.633	3.56
1_5	423	25.0	45.0	3.07	0.0207	0.173	0.0129	0.0236	0.0439	0.0591	0.371	0.704	3.40
1_6	423	50.0	90.0	2.04	0.0260	0.181	0.0190	0.0271	0.0521	0.0720	0.388	0.765	2.90
1_7	473	10.0	16.1	3.29	0.0170	0.111	0.00406	0.0159	0.0361	0.0546	0.243	0.482	2.77
1_8	473	25.0	40.3	2.74	0.0206	0.137	0.0102	0.0203	0.0388	0.0568	0.300	0.584	2.98
1_9	473	50.0	80.5	1.83	0.0281	0.153	0.0184	0.0257	0.0563	0.0794	0.335	0.696	2.35
<i>Monolith M2 (activated at 1333 K, 6 h)</i>													
2_1	373	10.0	20.4	4.17	0.117	0.178	0.179	0.278	0.413	0.345	0.604	2.11	-
2_2	373	25.0	51.0	3.48	0.123	0.186	0.183	0.288	0.416	0.350	0.612	2.16	-
2_3	373	50.0	102	2.32	0.132	0.197	0.193	0.310	0.423	0.361	0.621	2.24	-
2_4	423	10.0	18.0	3.68	0.109	0.152	0.172	0.258	0.357	0.312	0.484	1.84	-
2_5	423	25.0	45.0	3.07	0.117	0.163	0.179	0.272	0.368	0.325	0.509	1.93	-
2_6	423	50.0	90.0	2.04	0.127	0.177	0.187	0.300	0.390	0.352	0.547	2.08	-
2_7	473	10.0	16.1	3.29	0.101	0.127	0.166	0.236	0.297	0.276	0.379	1.58	-
2_8	473	25.0	40.3	2.74	0.106	0.136	0.173	0.248	0.304	0.290	0.398	1.65	-
2_9	473	50.0	80.5	1.83	0.117	0.164	0.182	0.301	0.327	0.318	0.452	1.86	-

(Continue on the next page)

Run	Temp. (K)	Total alkane pressure (kPa)	Total alkane flow rate ($\mu\text{mol.min}^{-1}$)	He flow rate (mL.min^{-1})	q_i (mol.kg^{-1})							q_{mix} (mol.kg^{-1})	S_s
					iC5	nC5	22DMB	23DMB	3MP	2MP	nC6		
<i>Monolith M3 (activated at 1333 K, 12 h)</i>													
3_1	373	10.0	20.4	4.17	0.145	0.202	0.309	0.423	0.565	0.488	0.745	2.88	-
3_2	373	25.0	51.0	3.48	0.153	0.217	0.319	0.453	0.588	0.512	0.781	3.02	-
3_3	373	50.0	102	2.32	0.166	0.240	0.341	0.483	0.314	0.543	0.816	3.20	-
3_4	423	10.0	18.0	3.68	0.128	0.174	0.298	0.388	0.484	0.433	0.605	2.51	-
3_5	423	25.0	45.0	3.07	0.137	0.189	0.304	0.411	0.506	0.450	0.636	2.63	-
3_6	423	50.0	90.0	2.04	0.145	0.204	0.320	0.438	0.525	0.473	0.656	2.76	-
3_7	473	10.0	16.1	3.29	0.111	0.146	0.262	0.332	0.385	0.363	0.449	2.05	-
3_8	473	25.0	40.3	2.74	0.120	0.162	0.281	0.362	0.417	0.390	0.490	2.22	-
3_9	473	50.0	80.5	1.83	0.128	0.180	0.304	0.393	0.451	0.419	0.527	2.40	-

The monoliths were packed in column 2 (see Chapter 3). Since the column has 0.12 m length and 0.01 m internal diameter, the packing was performed by wrapping the materials with inert glass wool in order to guarantee a fixed bed. The remaining space of the column was filled with small glass spheres;

The flow rates are expressed at STP conditions;

The elution order (sorption hierarchy) for monoliths M2 and M3 does not fit with the one from Eq.3.5 (see Chapter 3).

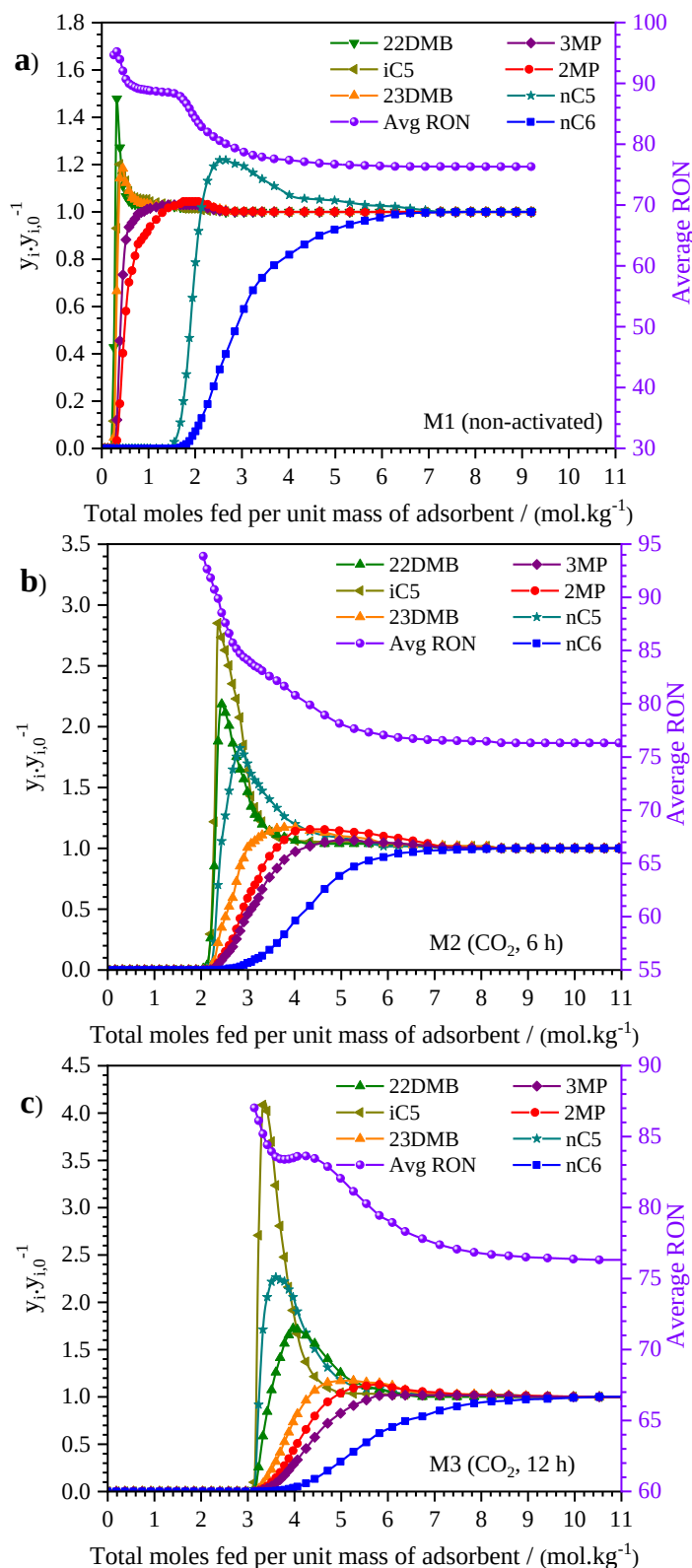


Figure 7.4 | Experimental breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in 3D-printed monoliths at 373 K and 50.0 kPa: a) M1, b) M2, and c) M3.

As it can be seen, the outcomes are completely different between the monoliths before and after the CO₂ activation process. For the monolith M1 (Figure 7.4a), the results indicate an adsorption hierarchy order as follows: nC6 > nC5 >>> 2MP > 3MP > 23DMB $\approx$ iC5 > 22DMB. Moreover, one can equally observe the ability of the material to separate the linear paraffins from its branched isomers via a near molecular sieving mechanism, similar to the effect shown by the benchmark molecular sieve zeolite 5A. The HRON molecules 22DMB/iC5/23DMB elute from the column at the very beginning of the experiments, closely followed by the mono-branched hexanes 3MP and 2MP. All the branched paraffins practically reach the saturation at a total molar amount fed of 0.5 mol.kg⁻¹, while the linear nC5 and nC6 start their elution only at 1.5 and 2.0 mol.kg⁻¹, respectively. To the best of our knowledge, the ability to completely separate linear and branched paraffins from complex pentane and hexane isomers mixtures has never been reported to such an extent before in any type of porous solid carbonaceous materials.

The size-selective separation of n/iso-paraffins arises due to the micropore morphology and connectivity of the monolith material. Generally, two different types of micropores can be present in amorphous microporous polymers, being defined as open and restricted access.³³ Micropores with narrow openings (restricted access), which cannot be easily accessible, are expected to be present next to open pores that are well connected and quickly filled. Consequently, the entrance to the restricted pores is narrow enough to allow the passage of the linear molecules, apparently under some diffusional limitations, while getting impassable by their branched counterparts, ultimately resulting in the molecular sieving effect. Moreover, one can see that 77.4% from the mixture loading (0.855 mol.kg⁻¹) corresponds to the adsorption of nC5 and nC6, suggesting a substantially higher volume in the micropores with restricted access, which might explain the small amounts of branched paraffins filled in the open pores.

On the other hand, both CO₂ activated monoliths (M2 and M3) do not exhibited such a size-exclusion separation. Figure 7.4b and 7.4c reveals that all paraffin isomers were adsorbed, with most of them practically showing a simultaneous elution at a total molar amount fed of 2.0 and 3.0 mol.kg⁻¹, respectively. Moreover, there is a change in the elution order of the components, with the pentane isomers leaving the column first. Also, a shift between the mono-branched hexanes 2MP and 3MP is seen. Therefore, for both monoliths M2 and M3, the adsorption hierarchy is equal to nC6 > 3MP > 2MP > 23DMB > 22DMB > nC5 > iC5, consistent to the normal boiling point order of the components. Another interesting remark seen in their breakthrough curves is the high overshoots in concentration, a typical characteristic of adsorption based on thermodynamically equilibrium competition. The least adsorbed

components are pushed out from the adsorbent by the more strongly adsorbed ones, and therefore their concentration sequentially rises above the feed. In the case of iC5, the rise in concentration can be more than 200% above that on the initial feed, clearly representing the strong competition of all components inside the monolithic structures.

Comparing the mixture loadings from each panel shown in Figure 7.4, the adsorption uptake achieved by the monolith M1 ($0.851 \text{ mol.kg}^{-1}$) is around three and four times lower than the ones obtained on the monoliths M2 (2.24 mol.kg^{-1}) and M3 (3.20 mol.kg^{-1}), respectively. This trend can be extended for the whole range of experimental conditions covered. These experimental findings are consistent with the characterization data reported in Table 7.1, such as $S_{\text{BET}}/Q_{\text{SDFIT}}$ and cumulative pore volume, which increases according to the degree of CO_2 activation. Moreover, according to Steldinger,³¹ despite creating additional microporosity, in the CO_2 activation process, there are also pore widening and joining of close pores (caused by the removal of the separating walls between them due to mass loss), being these effects more pronounced as temperature and/or activation time increases. This is probably the main reason why the molecular sieving separation seen in monolith M1 was not reproduced in the monoliths M2 and M3, since during the activation, pores sufficiently large were created to accommodate all alkane isomers, facilitating the adsorption of branched paraffins.

Practically, it can be concluded from the experimental observations that the monolith M1 represents the most suitable material considering applications for pentane and hexane isomer separation. Thus, an overview analysis of the effect of temperature and total alkane pressure on the septenary breakthrough curves measured on this material is provided in the following sections. Complete information on the experimental breakthrough curves performed on monoliths M2 and M3 are given in *Appendix E*.

7.3.2 Multicomponent Adsorption of Pentane and Hexane Isomers in Monolith M1

Figures 7.5, 7.6, and 7.7 show the breakthrough curves for the temperatures of 373, 423, and 473 K, respectively, plotted in terms of the normalized molar fraction ratio of each isomer as a function of time. In each figure, the effect of total alkane pressure is shown: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The real-time RON of the product mixture leaving the column is also illustrated. The results in these figures indicate that the size-selective separation of n/iso-paraffins is maintained for the entire range of working conditions. For instance, at 50 kPa, where

the mixture loadings are higher, the difference between the stoichiometric times of 2MP and nC5, last branched and first linear paraffin to elute from the column, respectively, is at least around 20 min. Moreover, the RON values reach a plateau at 89 when all branched paraffins leave the column separated from the linear alkanes, which is the same value achieved by the zeolite 5A in the TIP process.

Regarding the adsorption of linear paraffins, despite having the same kinetic diameter (0.43 nm), the nC6 molecule is preferentially adsorbed over the nC5, probably due to its longer linear chain that maximizes the contact surface area with the pore walls. The closer the molecules approach the pore walls, the higher the intensity of the interactions. Their equilibrium competition can result in feed concentration rising to 30% for the nC5. Additionally, the temperature does not strongly affect their breakthrough curves since a similar picture is observed when this variable increases. At a fixed total alkane pressure, their mass transfer zone width remains practically constant, as well as the magnitude of the overshoot for nC5.

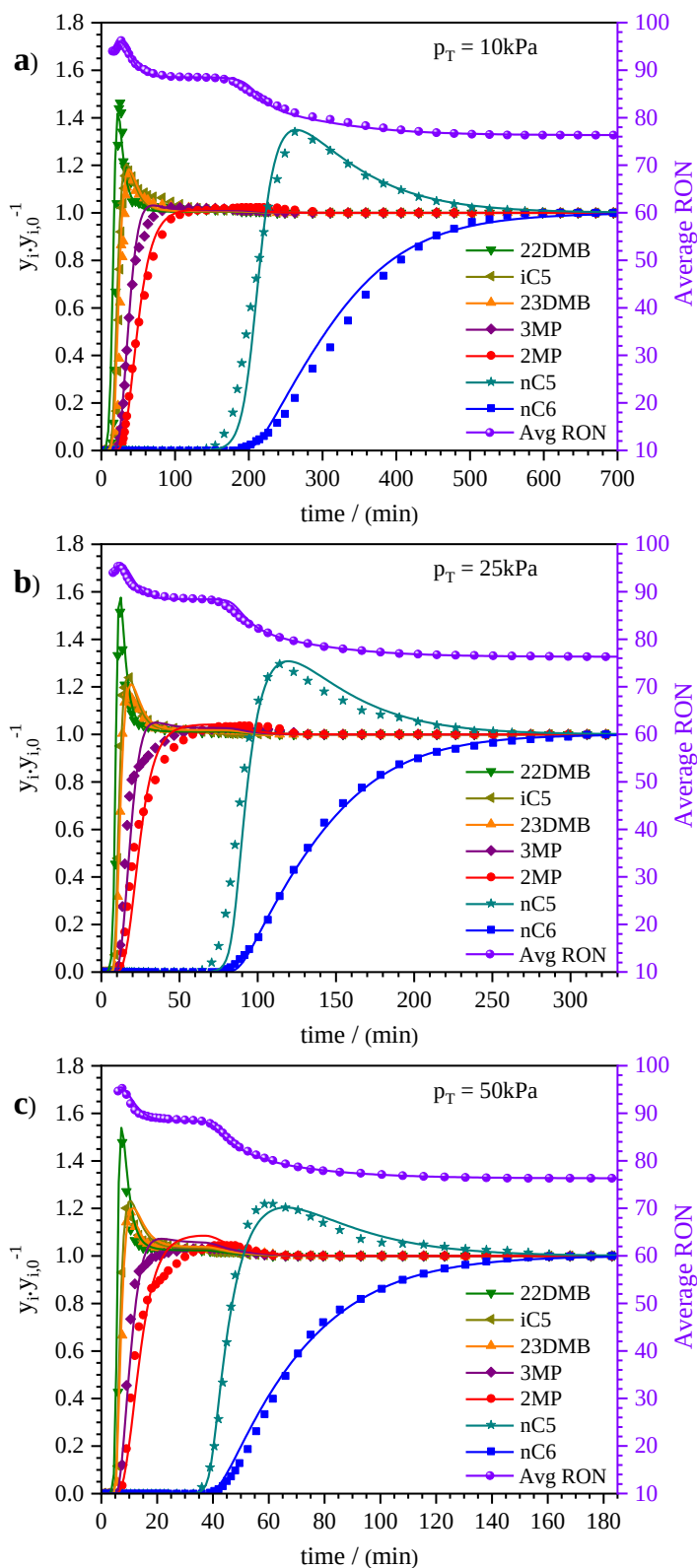


Figure 7.5 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 373 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

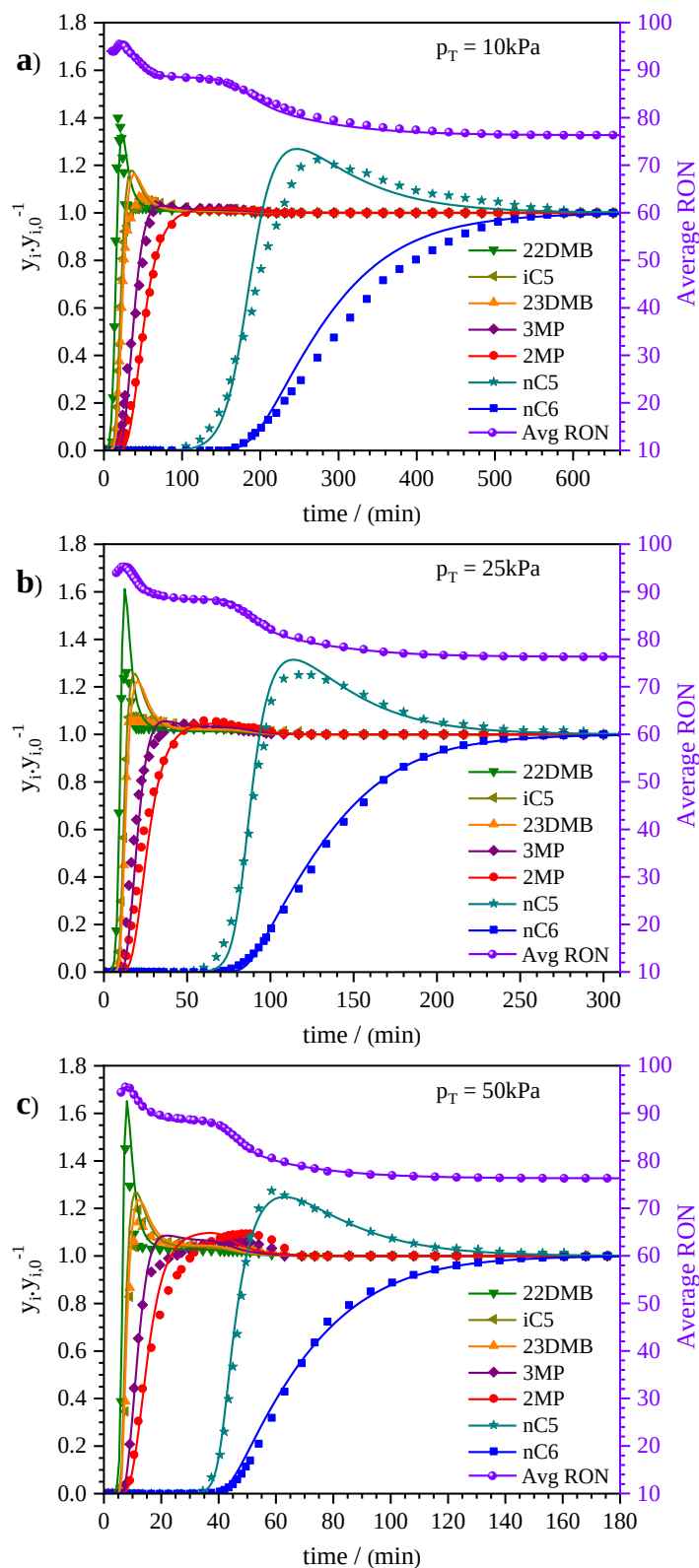


Figure 7.6 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 423 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

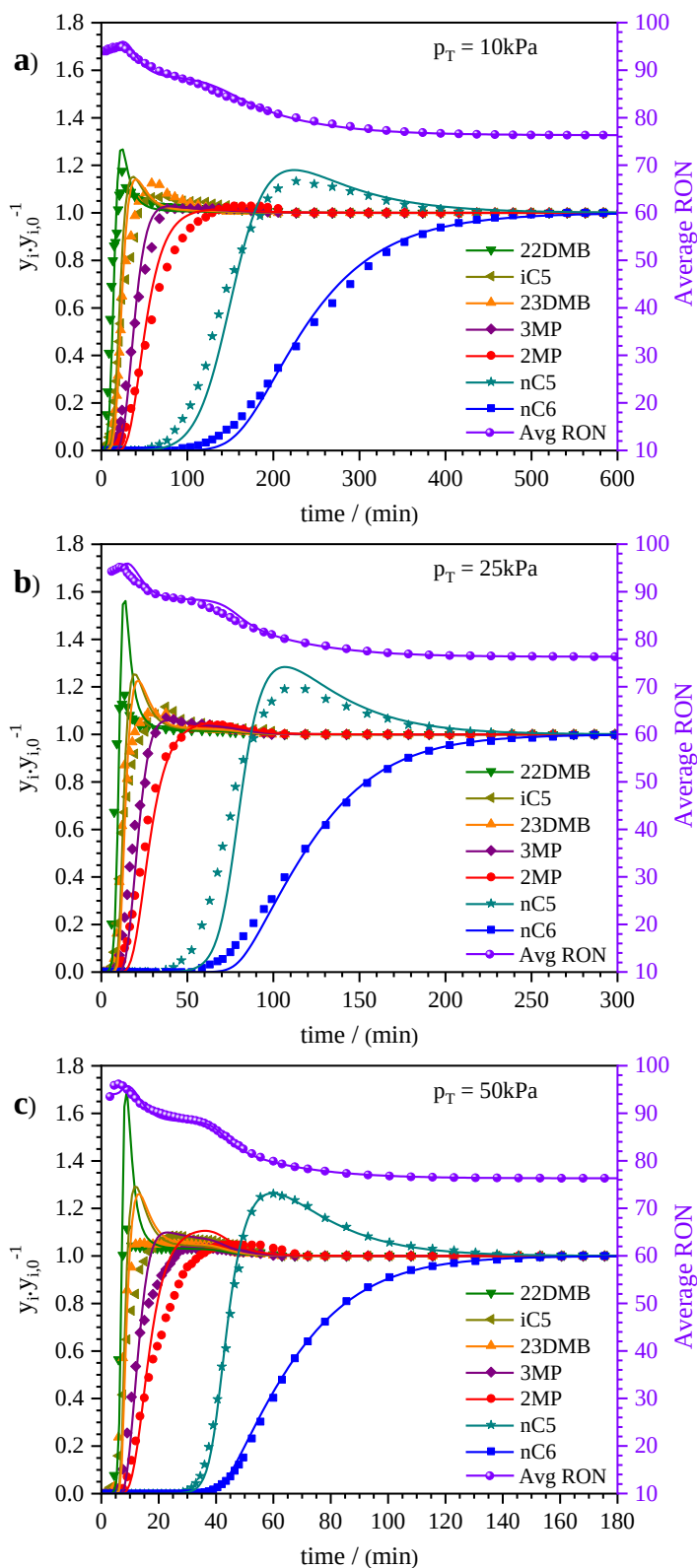


Figure 7.7 | Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 473 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa. The continuous lines represent the numerical simulations.

The sorption selectivities, also reported in Table 7.2, determined by the ratio of the loadings between linear over iso-paraffins (adapted from Eq. 3.5, *Chapter 3*), are given as a function of total alkane pressure in Figure 7.8. They slightly decrease with increasing temperature, ranging from around 3.7 at 373 K to 2.5 at 473 K. Moreover, they remain practically constant in the range of total alkane pressure studied.

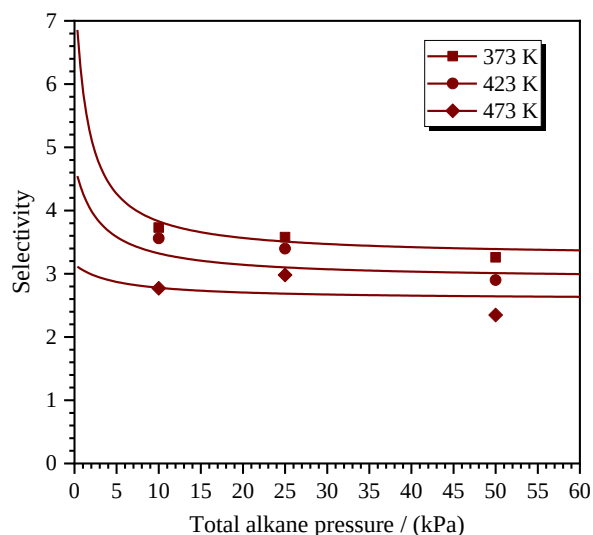


Figure 7.8 | Sorption selectivities of pentane and hexane isomers in monolith M1. The continuous lines represent the Langmuir model predictions.

The corresponding septenary adsorption equilibrium isotherms of pentane and hexane isomers in monolith M1 are shown in Figure 7.9. The selective separation between the loadings resulting from the sorption of n- and iso-paraffins is highlighted. Whatever the temperature studied, the isotherms are marked as type I according, reflecting their adsorption in the micropores of the material.³²

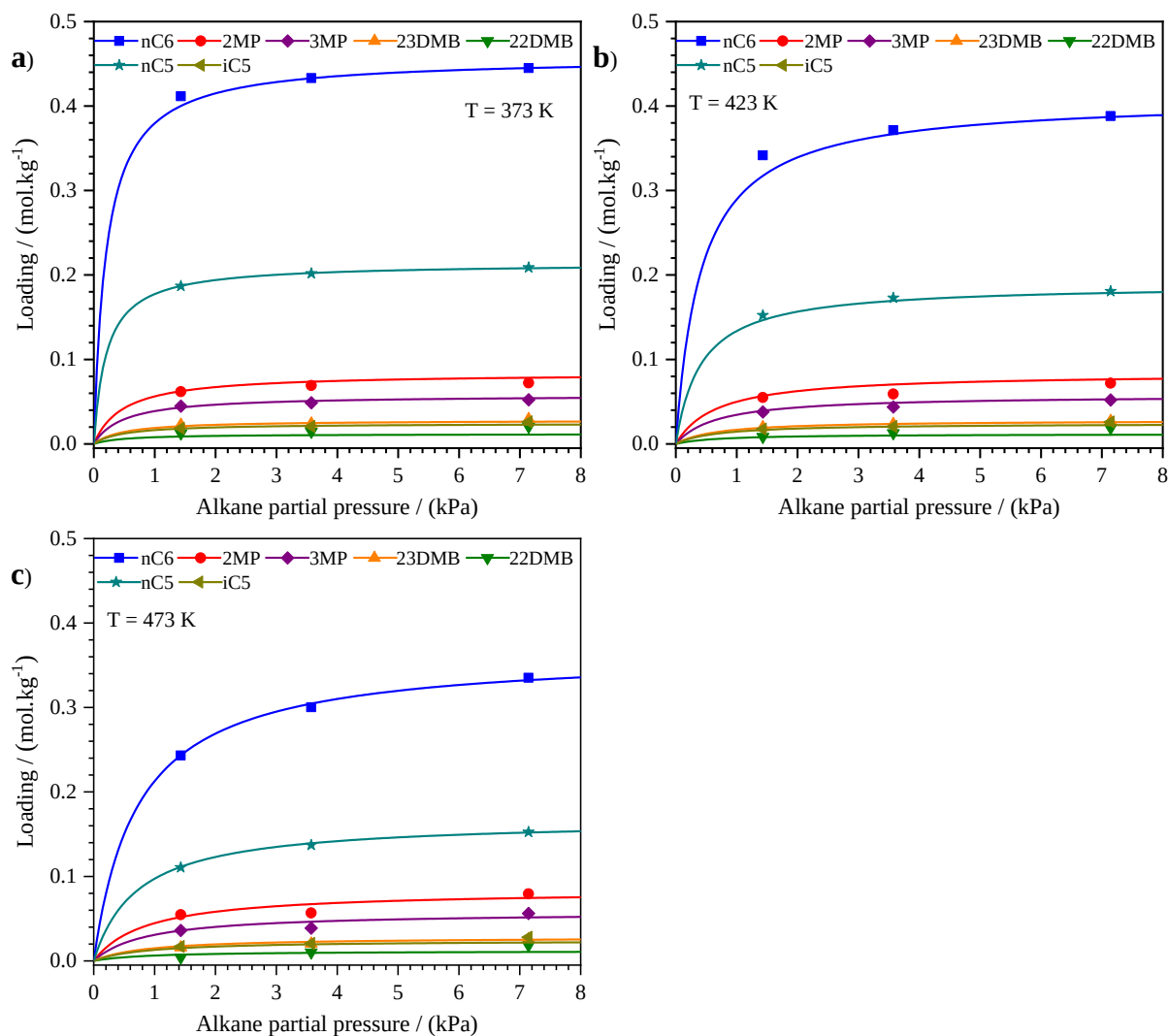


Figure 7.9 | Septenary adsorption equilibrium isotherms of pentane and hexane isomers in monolith M1: a) 373 K, b) 423 K, and c) 473 K. The continuous lines represent the Langmuir model predictions.

7.3.3 Modelling Adsorption Equilibrium Isotherms

The fitting results for the multicomponent septenary isotherms of pentane and hexane isomers in monolith M1 have already been shown in Figure 7.9 by the continuous lines. As exhibited, the adsorption equilibrium data was properly described. For the fitting procedure,

the loadings obtained from the breakthrough experiments (Table 7.2) were correlated with the Langmuir isotherm model described in *Chapter 3*. It can also be noted that the selectivities predicted by the model in Figure 7.8 show similar behaviour to the experimental ones.

Based on the size-selective separation of n/iso-paraffins resulting from the micropore topology of the monolith M1, we adopted the strategy to divide the sorption competition in the Langmuir isotherm into two groups. One accounts for the small amounts of branched paraffins in the open pores and the other for the adsorption of linear paraffins on the pores with restricted access. Moreover, we assumed that the linear nC5 and nC6 are only adsorbed in the narrow pores. These assumptions were made to simplify the fitting procedure, helping better represent the adsorption data. It seems valid since the breakthrough curves (Figures 7.5 - 7.7) do not evidence an equilibrium competition between n/iso-paraffins. Generally, when nC5 (first linear molecule to saturate) starts to elute from the column, the 2MP (last branched molecule to saturate) has already almost reached its feed concentration, and practically there is no displacement (overshoot phenomenon) of this mono-branched hexane associated with the advancement in the wavefront of the linear pentane.

The respective model parameters obtained from the fitting procedure are reported in Table 7.3. As indicated, the relative magnitudes of q_{sat} and b are consistent with the sorption hierarchy order observed in the breakthrough curves: nC6 > nC5 > 2MP > 3MP > 23DMB > iC5 > 22DMB. The q_{sat} for the adsorption of linear paraffins in the narrow pores were allowed to be temperature-dependent, in which we assumed that the effect of temperature is the same for nC5 and nC6, being δ equal to 0.872. Regarding the $-\Delta H$, values around 18.2 and 8.5 kJ.mol⁻¹ were found for the sorption of n- and iso-paraffins, respectively.

Table 7.3 | Langmuir isotherm parameters for the sorption of pentane and hexane isomers in monolith M1 and average deviation between model predictions and experimental data.

Langmuir Parameters		Pentane isomers		Hexane isomers				
		nC5	iC5	nC6	2MP	3MP	23DMB	22DMB
δ	(-)	0.872	-	0.872	-	-	-	-
$-\Delta H_i$	(kJ.mol ⁻¹)	18.5	8.53	18.2	8.56	8.56	8.55	8.51
<i>Temperature: 373 K</i>								
$q_{sat1,i}$	(mol.kg ⁻¹)	0.506	0.140	0.794	0.310	0.220	0.160	0.100
$b_{1,i}$	(kPa ⁻¹)	2.05	0.356	2.80	0.553	0.538	0.360	0.242
$H_{1,i}$	(mol.kg ⁻¹ .kPa ⁻¹)	1.04	0.0498	2.22	0.171	0.118	0.0576	0.0242
<i>Temperature: 423 K</i>								
$q_{sat2,i}$	(mol.kg ⁻¹)	0.450	0.140	0.706	0.310	0.220	0.160	0.100
$b_{2,i}$	(kPa ⁻¹)	1.01	0.257	1.40	0.399	0.388	0.260	0.175
$H_{2,i}$	(mol.kg ⁻¹ .kPa ⁻¹)	0.456	0.0360	0.987	0.124	0.0855	0.0416	0.0175
<i>Temperature: 473 K</i>								
$q_{sat3,i}$	(mol.kg ⁻¹)	0.400	0.140	0.628	0.310	0.220	0.160	0.100
$b_{3,i}$	(kPa ⁻¹)	0.581	0.199	0.809	0.309	0.300	0.201	0.135
$H_{3,i}$	(mol.kg ⁻¹ .kPa ⁻¹)	0.233	0.0279	0.509	0.0957	0.0661	0.0322	0.0135
$\Sigma \bar{\Delta}q$					0.0212			

The reference temperature used was $T_0 = 373$ K.

7.3.4 Numerical Simulations of Multicomponent Breakthrough Curves

The numerical simulations for the multicomponent breakthrough curves of pentane and hexane isomers in monolith M1, using the dynamic mathematical model described in *Chapter 3*, have already been shown in Figures 7.5 - 7.7 by the continuous lines.

As mentioned earlier, the sorption dynamics of n- and iso-paraffins occur under different conditions. While the branched alkanes can quickly fill the small portion of open pores, producing sharp breakthrough curves to approach the feeding concentration, the adsorption of linear alkanes takes place on the narrow pores, which might impose some diffusion limitations, ultimately resulting in more “diffuse” breakthrough curves. Therefore, the numerical simulations were conducted by adjusting two independent mass transfer coefficients (Eq. 3.22,

Chapter 3): one accounting for the overall sorption of n-paraffins ($k_{LDF,n}$) and the other for the sorption of iso-paraffins ($k_{LDF,iso}$).

The k_{LDF} coefficients found to obtain the best fit of the experimental data range from 0.0018 s^{-1} (373 K) to 0.0031 s^{-1} (473 K) for the linear paraffins, and from 0.018 s^{-1} (373 K) to 0.031 s^{-1} (473 K) for their branched counterparts. Their temperature dependence, which follows the Arrhenius equation (Eq. 3.23, *Chapter 3*), gave rise to an ΔE_i of 8 kJ.mol^{-1} for all alkane isomers. As it shows, the $k_{LDF,n}$ is one order of magnitude lower than $k_{LDF,iso}$, which seems fair considering the diffusional effects arising from the microporous morphology and connectivity of monolith M1. In addition, the simulations revealed that the system is isothermal.

As a whole, a good agreement between the numerical predictions and experimental observations was obtained for the range of working conditions covered. The shapes of the breakthrough curves were properly captured, being the width of the mass-transfer zone and the overshoots in concentration due to competitive adsorption qualitatively well described in most cases. These results indicate that the extended Langmuir isotherm, combined with a simple lumped kinetic mass transfer rate model, is adequate to comprehensively analyse the sorption phenomena of pentane and hexane isomers in the 3D-printed monolith.

All the model parameters used for the simulations of experimental multicomponent breakthrough curves are reported in Tables E.1 – E.3 of *Appendix E*.

7.4 Conclusions

We report here the first experimental study on the sorption of pentane and hexane isomers on a series of hierarchically structured 3D-printed porous carbons monoliths. Multicomponent breakthrough experiments with septenary feed mixtures demonstrated that the monolith M1 (non-activated) could completely separate linear (nC6/nC5) from iso-paraffins (2MP/3MP/23DMB/iC5/22DMB – barely adsorbed), in a broad range of working conditions, through a near molecular sieving effect arising from its micropore morphology and connectivity. The equilibrium data were correlated with the Langmuir isotherm model and fitted parameters used in the numerical simulations, which adequately described the experimental breakthrough curves with the use of distinct mass transfer coefficients for the micropores with open ($k_{LDF,iso}$) and restricted access ($k_{LDF,n}$).

The breakthrough experiments performed on the CO₂ activated monoliths M2 (1133 K for 6 h) and M3 (1133 K for 13 h) exhibited a much larger sorption capacity. All paraffins were adsorbed with a hierarchy order following the normal boiling point order of the compounds: nC₆ > 3MP > 2MP > 23DMB > 22DMB > nC₅ > iC₅. Consequently, mixture loadings around three and four times higher than those from M1 were obtained on monoliths M2 and M3, respectively.

Based on the outcomes from this work and concerning potential strategies for octane number enhancement, it would be worth performing further studies regarding the stage of CO₂ activation in the production of 3D-printed monoliths. An interesting idea might be to find such a combination of temperature and time to possibly increase the specific surface area by adding a new fraction of micropores without provoking significant pore widening (monoliths M2 and M3), focusing on enhancing the adsorption capacity of linear paraffins.

7.5 References

- (1) Jänchen, J.; Schumann, K.; Thrun, E.; Brandt, A.; Unger, B.; Hellwig, U. Preparation, Hydrothermal Stability and Thermal Adsorption Storage Properties of Binderless Zeolite Beads. *Int. J. Low-Carbon Technol.* **2012**, 7, 275–279.
- (2) Yu, L.; Gong, J.; Zeng, C.; Zhang, L. Synthesis of Binderless Zeolite X Microspheres and Their CO₂ Adsorption Properties. *Sep. Purif. Technol.* **2013**, 118, 188–195.
- (3) Belviso, C. *Zeolites - Useful Minerals*; IntechOpen, 2016.
- (4) Permyakova, A.; Skrylnyk, O.; Courbon, E.; Affram, M.; Wang, S.; Lee, U. H.; Valekar, A. H.; Nouar, F.; Mouchaham, G.; Devic, T.; De Weireld, G.; Chang, J. S.; Steunou, N.; Frère, M.; Serre, C. Synthesis Optimization, Shaping, and Heat Reallocation Evaluation of the Hydrophilic Metal–Organic Framework MIL-160(Al). *ChemSusChem* **2017**, 10, 1419–1426.
- (5) Valekar, A. H.; Lee, S. G.; Cho, K. H.; Lee, U. H.; Lee, J. S.; Yoon, J. W.; Hwang, Y. K.; Cho, S. J.; Chang, J. S. Shaping of Porous Metal-Organic Framework Granules Using Mesoporous γ -Alumina as a Binder. *RSC Adv.* **2017**, 7, 55767–55777.
- (6) Khabzina, Y.; Dhainaut, J.; Ahlhelm, M.; Richter, H. J.; Reinsch, H.; Stock, N.; Farrusseng, D. Synthesis and Shaping Scale-up Study of Functionalized UiO-66 MOF

- for Ammonia Air Purification Filters. *Ind. Eng. Chem. Res.* **2018**, *57*, 8200–8208.
- (7) Mallick, A.; Mouchaham, G.; Bhatt, P. M.; Liang, W.; Belmabkhout, Y.; Adil, K.; Jamal, A.; Eddaoudi, M. Advances in Shaping of Metal-Organic Frameworks for CO₂ Capture: Understanding the Effect of Rubbery and Glassy Polymeric Binders. *Ind. Eng. Chem. Res.* **2018**, *57*, 16897–16902.
- (8) McCrae, P. D. A.; Zhang, T.; Walker, D. R. B. Method of Making Shaped Activated Carbon. U.S. Patent 20030022787A1, 2003.
- (9) Shao, X.; Feng, Z.; Xue, R.; Ma, C.; Wang, W.; Peng, X.; Cao, D. Adsorption of CO₂, CH₄, CO₂/N₂ and CO₂/CH₄ in Novel Activated Carbon Beads: Preparation, Measurements and Simulation. *AIChE J.* **2011**, *57*, 3042–3051.
- (10) Sun, N.; Sun, C.; Liu, H.; Liu, J.; Stevens, L.; Drage, T.; Snape, C. E.; Li, K.; Wei, W.; Sun, Y. Synthesis, Characterization and Evaluation of Activated Spherical Carbon Materials for CO₂ Capture. *Fuel* **2013**, *113*, 854–862.
- (11) Rezaei, F.; Webley, P. Optimum Structured Adsorbents for Gas Separation Processes. *Chem. Eng. Sci.* **2009**, *64*, 5182–5191.
- (12) Rezaei, F.; Webley, P. Structured Adsorbents in Gas Separation Processes. *Sep. Purif. Technol.* **2010**, *70*, 243–256.
- (13) Govender, S.; Friedrich, H. B. Monoliths: A Review of the Basics, Preparation Methods and Their Relevance to Oxidation. *Catalysts* **2017**, *7*, 62.
- (14) Thakkar, H.; Eastman, S.; Hajari, A.; Rownaghi, A. A.; Knox, J. C.; Rezaei, F. 3D-Printed Zeolite Monoliths for CO₂ Removal from Enclosed Environments. *ACS Appl. Mater. Interfaces* **2016**, *8*, 27753–27761.
- (15) Lawson, S.; Li, X.; Thakkar, H.; Rownaghi, A. A.; Rezaei, F. Recent Advances in 3D Printing of Structured Materials for Adsorption and Catalysis Applications. *Chem. Rev.* **2021**, *121*, 6246–6291.
- (16) Thakkar, H.; Eastman, S.; Al-Naddaf, Q.; Rownaghi, A. A.; Rezaei, F. 3D-Printed Metal-Organic Framework Monoliths for Gas Adsorption Processes. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35908–35916.

-
- (17) Lawson, S.; Al-Naddaf, Q.; Newport, K.; Rownaghi, A.; Rezaei, F. Assessment of CO₂/CH₄ Separation Performance of 3D-Printed Carbon Monoliths in Pressure Swing Adsorption. *Ind. Eng. Chem. Res.* **2021**, *60*, 16445–16456.
- (18) Jandyal, A.; Chaturvedi, I.; Wazir, I.; Raina, A.; Ul Haq, M. I. 3D Printing – A Review of Processes, Materials and Applications in Industry 4.0. *Sustain. Oper. Comput.* **2022**, *3*, 33–42.
- (19) Thakkar, H.; Eastman, S.; Al-Mamoori, A.; Hajari, A.; Rownaghi, A. A.; Rezaei, F. Formulation of Aminosilica Adsorbents into 3D-Printed Monoliths and Evaluation of Their CO₂ Capture Performance. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7489–7498.
- (20) Couck, S.; Lefevre, J.; Mullens, S.; Protasova, L.; Meynen, V.; Desmet, G.; Baron, G. V.; Denayer, J. F. M. CO₂, CH₄ and N₂ Separation with a 3DFD-Printed ZSM-5 Monolith. *Chem. Eng. J.* **2017**, *308*, 719–726.
- (21) Couck, S.; Cousin-Saint-Remi, J.; Van der Perre, S.; Baron, G. V.; Minas, C.; Ruch, P.; Denayer, J. F. M. 3D-Printed SAPO-34 Monoliths for Gas Separation. *Microporous Mesoporous Mater.* **2018**, *255*, 185–191.
- (22) Thakkar, H.; Lawson, S.; Rownaghi, A. A.; Rezaei, F. Development of 3D-Printed Polymer-Zeolite Composite Monoliths for Gas Separation. *Chem. Eng. J.* **2018**, *348*, 109–116.
- (23) Lawson, S.; Rezaei, F. Effects of Process Parameters on CO₂/H₂ Separation Performance of 3D-Printed MOF-74 Monoliths. *ACS Sustain. Chem. Eng.* **2021**, *9*, 10902–10912.
- (24) Lawson, S.; Al-Naddaf, Q.; Krishnamurthy, A.; Amour, M. S.; Griffin, C.; Rownaghi, A. A.; Knox, J. C.; Rezaei, F. UTSA-16 Growth within 3D-Printed Co-Kaolin Monoliths with High Selectivity for CO₂/CH₄, CO₂/N₂, and CO₂/H₂ Separation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 19076–19086.
- (25) Grande, C. A.; Blom, R.; Middelkoop, V.; Matras, D.; Vamvakeros, A.; Jacques, S. D. M.; Beale, A. M.; Di Michiel, M.; Anne Andreassen, K.; Bouzga, A. M. Multiscale Investigation of Adsorption Properties of Novel 3D Printed UTSA-16 Structures. *Chem. Eng. J.* **2020**, *402*, 126166.
- (26) Lawson, S.; Griffin, C.; Rapp, K.; Rownaghi, A. A.; Rezaei, F. Amine-Functionalized

- MIL-101 Monoliths for CO₂ Removal from Enclosed Environments. *Energy and Fuels* **2019**, 33, 2399–2407.
- (27) Lawson, S.; Snarzyk, M.; Hanify, D.; Rownaghi, A. A.; Rezaei, F. Development of 3D-Printed Polymer-MOF Monoliths for CO₂ Adsorption. *Ind. Eng. Chem. Res.* **2020**, 59, 7151–7160.
- (28) Regufe, M. J.; Ferreira, A. F. P.; Loureiro, J. M.; Rodrigues, A.; Ribeiro, A. M. Electrical Conductive 3D-Printed Monolith Adsorbent for CO₂ Capture. *Microporous Mesoporous Mater.* **2019**, 278, 403–413.
- (29) Mendes, D. N. D. L.; Gaspar, A.; Ferreira, I.; Mota, J. P. B.; Ribeiro, R. P. P. L. 3D-Printed Hybrid Zeolitic/Carbonaceous Electrically Conductive Adsorbent Structures. *Chem. Eng. Res. Des.* **2021**, 174, 442–453.
- (30) Steldinger, H.; Esposito, A.; Brunnengräber, K.; Gläsel, J.; Etzold, B. J. M. Activated Carbon in the Third Dimension—3D Printing of a Tuned Porous Carbon. *Adv. Sci.* **2019**, 6, 1–9.
- (31) Steldinger, H. 3D Printing of Activated Carbon and Exemplary Application as Adsorbent in the Electric Swing Adsorption. PhD Thesis, Technische Universität Darmstadt, 2020.
- (32) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, 87, 1051–1069.
- (33) Jeromenok, J.; Weber, J. Restricted Access: On the Nature of Adsorption/Desorption Hysteresis in Amorphous, Microporous Polymeric Materials. *Langmuir* **2013**, 29, 12982–12989.

8 CONCLUSIONS AND FUTURE WORK

This thesis is structured into eight chapters, including a review of the state of the art, one describing the methodologies applied for screening the adsorbent materials, and four experimental chapters corresponding to the sorption studies on different kinds of MOFs: ZIF-8, MIL-140s (forms A, B, and C, and MIL-160(Al); and carbon-based structures (3D-printed monoliths) for the separation of pentane and hexane isomers mixtures into fractions of HRON and LRON compounds. In this final chapter, an overview of the major findings of this work is summarised. Finally, future work is also provided.

8.1 Overall Conclusions

This work was committed to studying new adsorptive materials with the potential to be applied in separation technologies for the complete fractionation of pentane and hexane isomers from light naphtha streams according to classes of HRON (iC5/22DMB/23DMB) and LRON (nC5/nC6/2MP/3MP) compounds. Thus, upgrading the current TIP process to achieve an unprecedented average RON of the final product of at least 92. For this purpose, different classes of adsorbent materials, including MOFs and 3D-printed carbon monoliths, were explored as alternatives to the benchmark molecular sieve zeolite 5A, which only separates linear from branched paraffins giving rise to a final RON in TIP processes of around 89. The greatest attention was delivered to MOFs due to their modular nature, which affords unique features that postulate them as the most promising candidates for the separation challenges of industrially valuable hydrocarbons.

Knowing that the development of an adsorption-based separation process requires detailed knowledge of the equilibrium and kinetics of adsorption and their impact on the dynamic response of a fixed bed adsorption column, a specific laboratory unit to collect breakthrough data concentration profiles in the gas phase was built, and a general mathematical model developed to guide and understand such information (*Chapter 3*). The literature review presented in *Chapter 2* revealed that most of the adsorption studies in this field using MOFs generally did not consider complex alkane feed mixtures, including both pentane and hexane isomers at temperatures above 373 K, therefore not represent the real conditions under the current industrial practice. Accordingly, to overcome this limitation and present reliable experimental data representative of the conventional TIP processes, the newly built fixed bed breakthrough apparatus was designed to enable working with feed mixtures of all these alkane isomers, from where several data were measured in different types of adsorbent materials.

The first material evaluated in this work was the MOF ZIF-8, *Chapter 4*. It is one of the first MOFs that have previously been studied with performance data showing some potential to compete and overcome the features of molecular sieves, such as the zeolite 5A to fractionate pentane and hexane isomers into fractions of HRON and LRON ones. Despite emerging as a potential alternative due to its higher adsorption capacity, until the present work, there is still a lack of information on ZIF-8 to understand its sorption behaviour completely, which motivated its selection in order to fill this gap in the literature and also validate the capability of the new breakthrough apparatus to collect reliable data. For the first time, the ZIF-8 material was

systematically evaluated through the measurement of breakthrough curves using feed mixtures of all the alkane isomers in the pentane and hexane range, together with numerical simulations that supported the experimental data giving insights into the governing sorption mechanisms. Our results disclosed a global sorption hierarchy order according to the degree of branching, $nC6 > nC5 > 2MP > 3MP > iC5 > 23DMB > 22DMB$, resulting from a mix of sorption mechanisms, it being thermodynamic driven for the linear alkanes and kinetically controlled for the corresponding branched ones, in which the higher the degree of branching is, the higher the diffusional limitations.

Through *Chapter 4*, it is demonstrated that the working conditions in fixed bed flow systems significantly impact the alkane isomers adsorption and separation in ZIF-8. Among them, the correct selection of the gas residence time in the column is crucial since it was observed that kinetic limitation effects are of fundamental importance, in which different pictures/separations can be obtained by changing its value. Very short residence times can lead to a complete exclusion of branched molecules, with the material acting as a molecular sieve for separating linear from branched paraffins, such as in zeolite 5A. It is also demonstrated that the increase of the residence time of the gas in the column results in the partial separation of branched hexane isomers, mono- (2MP/3MP) and di- (23DMB/22DMB), with a product mixture reaching RON values of at least 92 and ideal productivity up to $0.194 \text{ mol.dm}^{-3}$. When all pentane and hexane isomers are fed to the column, the partial separation of mono- (2MP/3MP/*i*C5) and di-branched (23DMB/22DMB) compounds is obtained with an ideal productivity up to $0.176 \text{ mol.dm}^{-3}$, which is practically the same.

The strong dependence between branched alkanes adsorption and gas residence time in the column severely complicates the laboratory and respective characterisation of the ZIF-8 material. This is so because the measured adsorption equilibrium data may not represent the true adsorption equilibrium and is only applicable to the particular system evaluated (using the so-called concept of pseudo adsorption equilibrium isotherms valid for the selected gas residence time at the inlet of the column). This phenomenon makes difficult the use of this material in the scale-up to cyclic industrial operations and requires further studies to appropriately tune the correct cycle time, for example, in a PSA. The complexity of ZIF-8 adsorption behaviour indeed represents a significant drawback for the development of an adsorption recycling technology in TIP processes. In addition, the very small value of the apparent particle density of ZIF-8 (0.325 g.cm^{-3}) means another obstacle to its use in industrial

applications once it substantially decreases the ideal productivity on a volume basis of this material.

A collaboration with *IMAP* allowed us to evaluate the potential of two other different kinds of MOF materials: the isorecticular series of Zr carboxylate MOFs MIL-140s (A, B, and C) and the Al dicarboxylate MIL-160(Al).

The MIL-140s (A, B, and C) studied in *Chapter 5* represent a prominent example of fine-tuning the pore size through a topologically directed material design, and our data highlighted the powerfulness of this strategy for developing new adsorbents for specific separations. While the sorption of hexane isomers in MIL-140A and C, constructed from the smallest and largest aromatic dicarboxylate linkers, respectively, resulted in poor selectivity, the data obtained in MIL-140B are of interest. The material exhibited a thermodynamically-driven separation of hexane isomers by classes of linear (nC6) > mono-branched (2MP/3MP) > di-branched (23DMB/22DMB), achieving a 92 RON ideal productivity up to 0.801 mol.dm⁻³, which is higher than previous values reported for other materials in literature (Figure 8.1). However, the results were limited to the low/moderate temperature of 343 K, meaning that an improvement should be made for the MOF to be capable of keeping its separation performance at higher temperatures, interesting for industrial operation. Another important fact that can be retained, as also demonstrated in other materials such as Fe₂(BDP)₃ and Zn₉(tba)₉(dabco)₃ (see *Chapter 2*), is that a one-dimensional triangular pore shape might be a good molecular-level descriptor for designing novel porous adsorbents for hexane isomer separation.

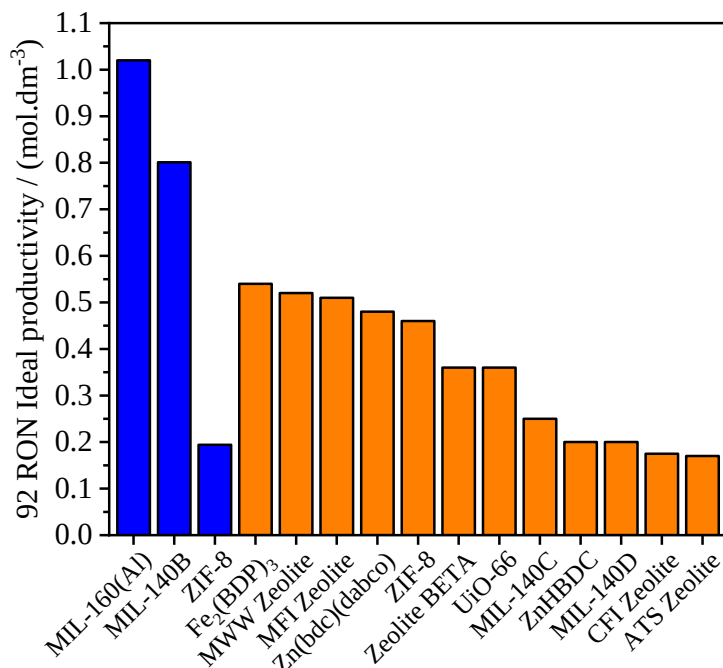


Figure 8.1 | Comparison of the 92 RON ideal productivities for separating equimolar quinary mixtures of hexane isomers using various materials. The blue columns represent the experimental data obtained in our laboratory for MIL-160(Al) and ZIF-8 at 423 K and total alkane pressure of 50 kPa, and for MIL-140B at 343 K and 50 kPa. All other columns in orange stand for the data from literature reported by Herm et al. (*Chapter 2*), which are based on CBMC simulations performed at 433 K and 100 kPa, and calculated using the respective framework density of each material.

In *Chapter 6*, a new adsorptive process, presented in Figure 8.2, for recovering HRON paraffins from light naphtha fractions was proposed, which led to an experimentally and unprecedented final product with a 92 RON ideal productivity of 1.14 mol.dm⁻³. The core of the innovative technology with considerable potential for the refining industry relies on the complementary role played by the MOF MIL-160(Al) and the benchmark zeolite 5A integrated into a mixed-bed adsorber. Studies performed in a single bed of MIL-160(Al) revealed the distinctive ability of the material to efficiently separate through thermodynamic mechanisms the hexane isomers in valuable fractions according to the degree of branching, linear (nC6) >> mono-branched (2MP/3MP) >> and di-branched (23DMB/22DMB) with an associated 92 RON ideal productivity up to 1.02 mol.dm⁻³ that surpasses the potential materials reported in the literature (Figure 8.1). In addition, the material has the unique ability to separate all HRON from the LRON branched alkanes with a hierarchy sorption order, 2MP > 3MP >> 23DMB > iC5 > 22DMB, that differs from other potential candidates, such as Fe₂(BDP)₃, ZIF-77, and also ZIF-8, which showed that the HRON (iC5) elutes with or closer to the LRON fraction of mono-branched hexanes, thus preventing maximising the improvement in the TIP process. Unfortunately, the MIL-160(Al) material cannot be used as a sole adsorbent due to the

practically simultaneous elution of the LRON nC5 with 23DMB in the HRON fraction, considerably decreasing the overall process performance. However, this issue could be easily overcome by incorporating into the bed the commercially available zeolite 5A (proportion of 70 wt.% MOF / 30 wt.% zeolite) that displaced the nC5 forward to the LRON fraction of mono-branched hexanes 3MP and 2MP due to its molecular sieving behaviour. As a result, the following ideal sorption hierarchy order was obtained $nC6 > nC5 > 2MP \approx 3MP \gg 23DMB > iC5 \approx 22DMB$, associated with an exceptional 92 RON ideal productivity that goes up to 1.14 mol.dm^{-3} . As far as our knowledge goes, this is the first time all the pentane and hexane isomers were efficiently separated into valuable fractions of HRON and LRON under relevant industrial working conditions, filling the gap in the current industrial adsorption separation science.

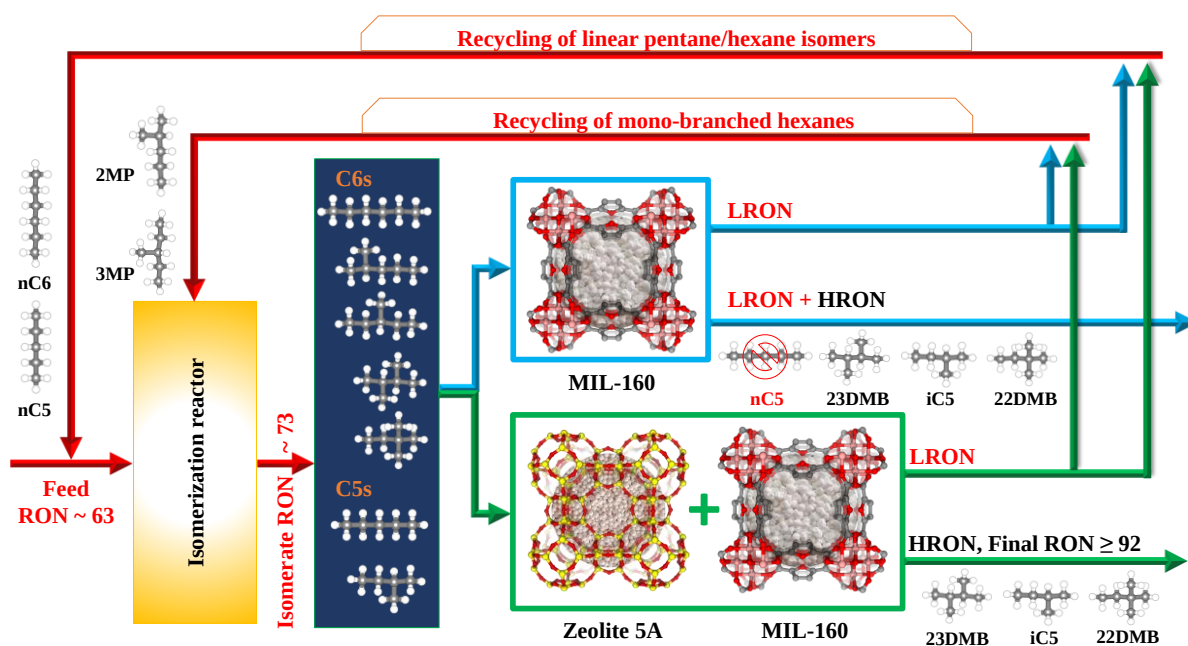


Figure 8.2 | Schematic representation of the new recycling technology for TIP processes using a mixed-bed adsorption of MOF MIL-160(Al) and zeolite 5A to fractionate the pentane and hexane isomers reactor output into a final HRON (≥ 92) isomerate product and an LRON recycle effluent fraction.

The timeline shown in *Chapter 2* covering the most representative breakthrough progressions in the field using MOFs can now be updated with the findings obtained in this work for ZIF-8, MIL-140B, and MIL-160(Al) materials, as can be seen in Figure 8.3.

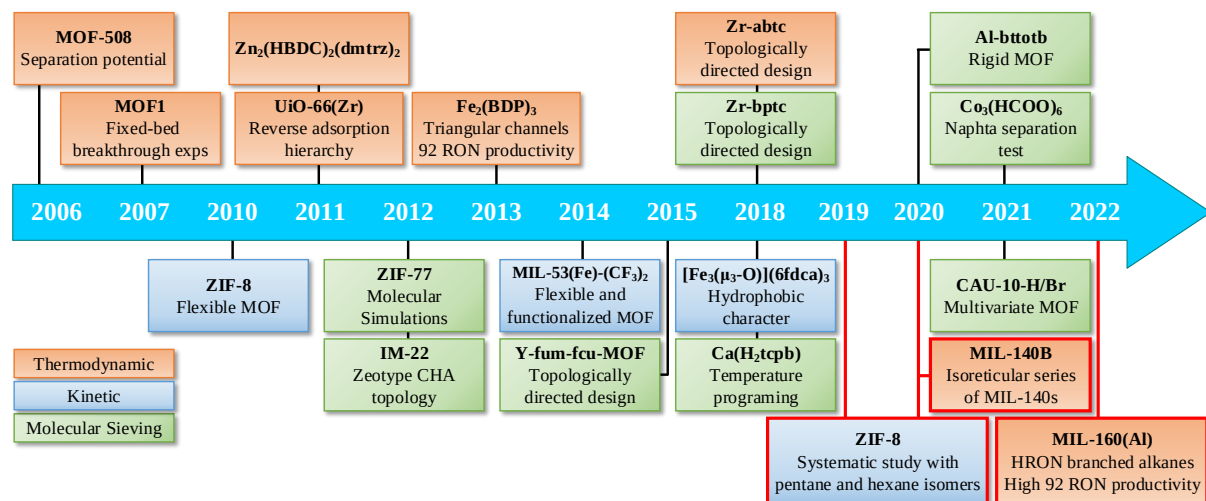


Figure 8.3 | Updated timeline of significant breakthroughs for MOFs in the field of pentane and hexane isomer separation. Data from this work are highlighted in red.

A collaboration with *Technische Universität Darmstadt* allowed us to test the potential of porous carbons monoliths for separating pentane and hexane isomers. The study shown in *Chapter 7* outlines the first work dealing with hierarchically structured materials in the third dimension for this specific separation target. Among the three materials screened, M1 (non-activated), M2 (CO₂ activated at 1133 K for 6 h), and M3 (CO₂ activated at 1133 K for 12 h), interesting data were obtained in the non-activated monolith, which could separate linear from iso-paraffins, through a near molecular sieving mechanism, in a relevant range of temperature. However, it presented a relatively low adsorption capacity for the linear alkanes. Nevertheless, it was shown that the CO₂ activation process yielded an additional microporosity fraction for the monoliths M2 and M3, accompanied by pore widening. Therefore, it seems reasonable to hypothesise that a “softer” activation stage, i.e., lowering the time or the temperature, or even a combination of both, might increase the microporosity of the 3D-printed monolith without provoking significant pore widening that compromises the separation of n/iso-paraffins, thus enhancing the adsorption capacity of linear alkanes. Or, in an ideal scenario, facilitate only the adsorption of LRON mono-branched hexanes 2MP and 3MP. We believe that the experimental findings from this work can contribute to producing improved porous carbon-based materials through the SLA 3D print technique.

As a final conclusion, the present PhD thesis constitutes an important reference in the adsorption field regarding the development of new separation processes from an engineering perspective. It comprises valuable tools and different strategies that can be addressed for a proper process design, besides encompassing examples of the different adsorption separation mechanisms (kinetic, thermodynamic equilibrium, and molecular sieving effects). Moreover, it highlights that, although it is a time-consuming method, the screening of an adsorbent material should always be accompanied by experimental evidence. As demonstrated throughout this work, the findings for the adsorption of hexane isomers in ZIF-8 and MIL-140B deviated/contradicted the previous CBMC results for these materials. This happens because some intrinsic features of the system can only be observed through laboratory experimentation. Finally, it shows the importance of mathematical modelling to analyse and interpret experimental observations, giving insights into the governing sorption mechanisms, especially when diffusional limitations are present. Still, it can also be retained that a dynamic mathematical model constructed based on simple but reliable adsorption isotherms and mass transfer rate models can provide a comprehensive understanding of the system under study.

8.2 Future Work

Future work should be directed to scale up the new adsorptive separation technology developed based on the synergistic action of MOF MIL-160(Al) and zeolite 5A (Figure 8.2) to an industrial stage. MIL-160(Al) has a superior 92 RON separation performance than other materials and can be produced at a multi-kilogram scale through an environmentally friendly synthesis method with cheap and readily available raw materials. At the same time, zeolite 5A is already commercially available. These features render the building block for further testing at a pilot scale. Given that, the mathematical model presented in *Chapter 3* should be upgraded with the prospects of simulating in a continuous cyclic mode in order to design and optimise the pilot plant operation.

Appendix A

A.1 Literature Review of Experimental Studies on the Adsorption and Separation of Pentane and Hexane Isomers in MOFs

Table A.1 shows an extensive review of the experimental works applying MOF materials for the adsorptive separation of pentane and hexane isomers over the past decades, since the first report by Chen et al.¹ in 2006. The contents of the Table comprise the main characteristics of the materials (structure and channel dimensions), the experimental technique approached (pulse experiments, breakthrough curves, and adsorption equilibrium isotherms) together with the range of working conditions and the alkanes considered, and also, the primary separation mechanism governing the sorption behaviour (thermodynamic, kinetic, and molecular sieving effect). The most significant breakthrough achievements reached over these years were highlighted and discussed in *Chapter 2*.

Table A.1 | Experimental studies of adsorption and separation of pentane and hexane isomers in MOFs.

MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
MOF-508	Topology: pcu 1D channels with 0.40 x 0.40 nm S_{Lang} : 946 m ² .g ⁻¹	Pulse gas chromatography from 393 K to 433 K - binary mixture: nC6/nC5, nC5/iC5 - ternary mixture: nC6/2MP/22DMB - quinary mixture: nC6/2MP/22DMB/nC5/iC5	Thermodynamic	1
MOF1	Topology: pcu, Two types of 3D intersecting channels with 0.75 x 0.75 nm and 0.38 x 0.47 nm	Adsorption equilibrium isotherms at 313 K and 343 K - single component: nC6, 3MP, 22DMB Multicomponent breakthrough curves at 313 K: - binary mixture: nC6/22DMB, nC6/3MP, 3MP/22DMB - ternary mixture: nC6/3MP/22DMB	Thermodynamic	2
MIL-47	1D lozenge channels with 0.85 nm	Pulse gas chromatography in the range of 393 K – 513 K - single component: nC6, 2MP, 23DMB, 22DMB, nC5, iC5	Thermodynamic	3
amino-MIL-53(Al)	1D lozenge channels with ≈0.6 nm	Pulse gas chromatography in the range of 285 K – 523 K - single component: nC6, 2MP, 3MP, 23DMB, 22DMB, nC5, iC5	Thermodynamic	4
Zn ₂ (HBDC) ₂ (dmtrz) ₂	Topology: pcu 1D channels with 0.67 x 0.67 nm S_{Lang} : 808 m ² .g ⁻¹ , S_{BET} : 552 m ² .g ⁻¹	Adsorption equilibrium isotherms at 298 K - single component: nC6, 3MP, 22DMB. Pulse gas chromatography at 343 K - single component: nC6, 3MP, 22DMB - ternary mixture: nC6/3MP/22DMB	Thermodynamic	5
UiO-66(Zr)	Topology: fcu An array of octahedral (1.1 nm) and tetrahedral (0.8 nm) cages accessible through triangular windows with ≈0.5 – 0.7 nm S_{BET} : 1002 m ² .g ⁻¹	Multicomponent breakthrough curves in the range of 343 K - 473 K - quaternary mixture: nC6/3MP/23DMB/22DMB	Thermodynamic	6

(Continue on the next page)

MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
UiO-66(Zr)-(Br) UiO-66(Zr)-(NO ₂) UiO-66(Zr)-(NH ₂)	S_{Lang} : 640 - 890 m ² .g ⁻¹ S_{BET} : 600 - 670 m ² .g ⁻¹ Pore volume: 0.7 - 1.0 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 343 K and 423 K - quaternary mixture: nC6/3MP/23DMB/22DMB	Thermodynamic	7
ZIF-76	Topology: lta Large cages accessible through eight membered ring windows. S_{BET} : 1560 m ² .g ⁻¹ Pore volume: 0.60 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 398 K: - binary mixture: nC6/3MP, nC6/22DMB, 3MP/22DMB	Thermodynamic	8
MIL-100(Fe) MIL-100(Cr)	Topology: mtm Two types of mesoporous cages (2.5 and 2.9 nm) accessible through pentagonal (0.55 nm) and hexagonal windows (0.86 nm) S_{BET} (Fe): 2040 m ² .g ⁻¹ S_{BET} (Cr): 2153 m ² .g ⁻¹	Pulse gas chromatography in the range of 353 K – 413 K - quinary mixture: nC6/2MP/23DMB/22DMB/cycleC6	Thermodynamic	9
MIL-100(Cr)	S_{BET} : 2400 m ² .g ⁻¹ Pore volume: 1.2 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 343K and 383 K - quaternary mixture: nC6/3MP/23DMB/22DMB	Thermodynamic	10
MOF-CJ3	1D tubular channels with 1.16 x 1.16 nm S_{BET} : 525 m ² .g ⁻¹	Pulse gas chromatography at 313 K: - quaternary mixture: nC6/2MP/22DMB/nC5	Thermodynamic	11
Fe ₂ (BDP) ₃	1D triangular channels with 0.49 nm S_{BET} : 1230 m ² .g ⁻¹	Adsorption equilibrium isotherms at 403 K, 433 K, 473 K - single component: nC6, 2MP, 3MP, 23DMB, 22DMB Multicomponent breakthrough curves at 433 K - quinary mixture: nC6/2MP/3MP/23DMB/22DMB	Thermodynamic	12

(Continue on the next page)

MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
MIL-125(Ti)-NH ₂	Two types of cages, octahedral (1.25 nm) and tetrahedral (0.61 nm), accessible through triangular windows with $\approx 0.5 - 0.7$ nm S_{BET} : 1550 m ² .g ⁻¹ Pore volume: 0.5 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 373K and 423 K - quaternary mixture: nC6/3MP/23DMB/22DMB	Thermodynamic	10
Al-fumarate	1D lozenged channels with 0.58 nm S_{BET} : 879.5 m ² .g ⁻¹ Pore volume: 0.48 cm ³ .g ⁻¹	Pulse gas chromatography at 483 K: - ternary mixture: nC6/3MP/23DMB	Thermodynamic	13
MIL-101(Cr)	Two types of mesoporous cages (2.7 and 3.4 nm) accessible through pentagonal (1.2 nm) or hexagonal windows (1.6 nm) S_{BET} : 3990 m ² .g ⁻¹	Adsorption equilibrium isotherms at 313 K - single component: nC6, 2MP, 23DMB, 22DMB. Pulse gas chromatography at 463 K: - quaternary mixture: nC6/2MP/23DMB/22DMB	Thermodynamic	14
COK-18	3D hierarchical pore system with micro- and mesopores S_{Lang} : 1048 m ² .g ⁻¹ , S_{BET} : 800 m ² .g ⁻¹ Pore volume: 0.45 cm ³ .g ⁻¹	Pulse gas chromatography at 483 K: - 11-component mixture: C1-C6 isomers	Thermodynamic	15
Zr-abtc	Topology: scu 1D channels with 0.70 nm S_{BET} : 1318 m ² .g ⁻¹ Pore volume: 0.45 cm ³ .g ⁻¹	Adsorption equilibrium isotherms in the range of 303 K - 423 K - single component: nC6, 3MP, 23DMB Multicomponent breakthrough curves at 303K and 423 K - ternary mixture: nC6/3MP/22DMB	Thermodynamic	16
DiaMM-1 DiaMM-2	Two types of tetrahedral cages accessible through triangular windows of 0.8 nm DiaMM-1 cages diameter: 0.75 and 0.91 nm DiaMM-2 cages diameter: 0.72 and 0.88 nm	Adsorption equilibrium isotherms at 293 K - single component: nC6, 2MP, 3MP, 23DMB Pulse gas chromatography in the range of 363 K - 423 K - senary mixture: nC5/nC6/2MP/3MP/23DMB/22DMB	Thermodynamic	17

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MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
Zn ₉ (tba) ₉ (dabco) ₃	Topology: bcu Two types of channels, triangular and quadrilateral, with edge diameters of 1.19 and 0.73 nm, respectively. S _{BET} : 1175 m ² .g ⁻¹ Pore volume: 0.64 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 298 K: - single component: nC6, 3MP, 23DMB, 22DMB Multicomponent breakthrough curves in the range 298K - 423 K - binary mixture: nC6/22DMB, 3MP/22DMB - ternary mixture: nC6/3MP/22DMB	Thermodynamic	18
CAU-10-H	Square shaped sinusoidal channels with periodic narrow (0.62 nm) and wide accesses (1.16 nm) S _{BET} : 483 m ² .g ⁻¹	Adsorption equilibrium isotherms at 303K: - single component: nC6, 3MP, 23DMB Multicomponent breakthrough curves at 303K, 333 K, and 363 K - ternary mixture: nC6/3MP/22DMB	Thermodynamic	19
Zn(BPZ) Zn(Me ₂ BPZ) Zn(BPZ(NH ₂) ₂)	Topology: sra 1D square channels with sizes ranging from 0.53 to 0.72 nm S _{BET} : 123 - 572 m ² .g ⁻¹	Pulse gas chromatography at 453 K, 463 K, 473 K: - single component: nC6, 2MP, 3MP, 23DMB, 22DMB	Thermodynamic	20
ZIF-8	Topology: sod Sodalite cages (1.14 nm) interconnected through flexible six-membered ring windows with 0.34 nm. S _{BET} : 1641 m ² .g ⁻¹	Pulse gas chromatography at 443 K: - quaternary mixture: nC6/2MP/23DMB/22DMB	Kinetic	21
ZIF-8	S _{BET} : 1813 m ² .g ⁻¹ Pore volume: 0.65 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 398 K: - binary mixture: nC6/3MP, nC6/22DMB, 3MP/22DMB	Kinetic	8
ZIF-8	S _{BET} : 1950 m ² .g ⁻¹ Pore volume: 0.66 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 313 K, 373 K, and 423 K - single component: nC6 Multicomponent breakthrough curves at 313 K, 373 K, and 423 K - binary mixture: 3MP/22DMB - ternary mixture: nC6/3MP/22DMB	Kinetic	22

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MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
ZIF-8	S_{BET} : 1971 m ² .g ⁻¹ Pore volume: 0.75 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 303 K, 343 K, and 373 K - single component: nC5, iC5 Multicomponent breakthrough curves at 343 K, 363 K, and 393 K: - binary mixture: nC5/iC5	Kinetic	23
ZIF-8	S_{BET} : 1800 m ² .g ⁻¹ Pore volume: 0.73 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 373 K - single component: nC6, 3MP, 23DMB, 22DMB	Kinetic	24
ZIF-8	S_{Lang} : 1927 m ² .g ⁻¹ S_{BET} : 1615 m ² .g ⁻¹	Adsorption equilibrium isotherms at 323 K - single component: nC6, 3MP, 23DMB	Kinetic	25
MIL-53(Fe)-(CF ₃) ₂	1D lozenge channels with narrow pore form with 0.42 nm and large pore form with 0.56 nm	Adsorption equilibrium isotherms at 313 K - single component: nC6, 3MP, 22DMB Multicomponent breakthrough curves at 313 K, 373 K, and 423 K - binary mixture: nC6/22DMB, 3MP/22DMB - ternary mixture: nC6/3MP/22DMB	Kinetic	26
[Fe ₃ (μ ₃ -O)](6FDCA) ₃	Quadrilateral channels with 0.8 x 1.29 nm S_{Lang} : 341 m ² .g ⁻¹ S_{BET} : 270 m ² .g ⁻¹ Pore volume: 0.21 cm ³ .g ⁻¹	Adsorption equilibrium isotherms in the range 298 K - 343 K - single component: nC6, 3MP, 22DMB Multicomponent breakthrough curves at 298 K - binary mixture: nC6/3MP, nC6/22DMB, 3MP/22DMB	Kinetic	27
Zn-adtb	Topology: scu 1D flexible channels with 0.65 nm S_{BET} : 273 m ² .g ⁻¹	Adsorption equilibrium isotherms at 303 K, 333 K, and 363 K - single component: nC6, 3MP, 23DMB Multicomponent breakthrough curves at 303 K - ternary mixture: nC6/3MP/22DMB	Kinetic	28

(Continue on the next page)

MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
IM-22	Topology: cha Cages interconnected through six-membered ring windows S_{BET} : 575 m ² .g ⁻¹ Pore volume: 0.24 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 398 K: - binary mixture: nC6/3MP, nC6/22DMB, 3MP/22DMB	Molecular sieving	8
MIL-127(Fe)	Topology: soc 1D channels with 0.60 nm and cages ($\approx$ 1.0 nm) through windows of 0.30 nm S_{BET} : 1400 m ² .g ⁻¹ Pore volume: 0.70 cm ³ .g ⁻¹	Multicomponent breakthrough curves at 343K, 373 K, and 423 K - quaternary mixture: nC6/3MP/23DMB/22DMB	Molecular sieving	10
Y-fumarate-fcu-MOF	Topology: fcu Interconnected octahedral and tetrahedral cages accessible through triangular windows with 0.47 nm S_{BET} : 691 m ² .g ⁻¹ Pore volume: 0.28 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 293 K: - single component: nC4, iC4, nC5, iC5 Multicomponent breakthrough curves at 298 K: - binary mixture: nC4/iC4	Molecular sieving	29
Ca(H ₂ tcpb)	1D flexible channels with $\approx$ 0.55 nm S_{BET} : 220 m ² .g ⁻¹	Adsorption equilibrium isotherms in the range of 303 K - 423 K - single component: nC6, 3MP, 22DMB, nC5, iC5 Multicomponent breakthrough curves at 363 K and 393 K - binary mixture: nC6/3MP, 3MP/22DMB, - ternary mixture: nC6/3MP/22DMB	Molecular sieving	30
Zr-bptc	Topology: ftw Cubic cage-like pores ($\approx$ 1.2 nm) interconnected through smaller tetrahedral cages with a windows size of 0.45 nm S_{BET} : 1030 m ² .g ⁻¹ Pore volume: 0.38 cm ³ .g ⁻¹	Adsorption equilibrium isotherms in the range of 303 K - 513 K - single component: nC6, 3MP, 23DMB Multicomponent breakthrough curves at 303K and 423 K - ternary mixture: nC6/3MP/22DMB	Molecular sieving	16

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MOF	MOF properties	Experimental methods and working conditions	Main separation mechanism	Ref
Al-bttotb	Two types of 1D channels with uniform size of 0.56 nm S_{BET} : 572 m ² .g ⁻¹ Pore volume: 0.22 cm ³ .g ⁻¹	Adsorption equilibrium isotherms at 303 K: - single component: nC6, 3MP, 22DMB Multicomponent breakthrough curves at 303 K - ternary mixture: nC6/3MP/22DMB - quinary mixture: nC6/3MP/2MP/23DMB/22DMB	Molecular sieving	31
CAU-10-Br	Square shaped sinusoidal channels with periodic narrow (0.54 nm) and wide accesses (1.16 nm)	Adsorption equilibrium isotherms at 303K - single component nC6, 3MP, 23DMB Multicomponent breakthrough curves at 303K, 333 K, and 363 K - ternary mixture: nC6/3MP/22DMB	Molecular sieving	19
CAU-10-H/Br	Square shaped sinusoidal channels with periodic narrow (0.41 nm) and wide accesses (1.16 nm) S_{BET} : 463 m ² .g ⁻¹	Adsorption equilibrium isotherms at 303K, 333 K, and 363 K - single component: nC6, 3MP, and 23DMB Multicomponent breakthrough curves at 303K, 333 K, and 363 K - binary mixture: nC6/22DMB, 3MP/22DMB - ternary mixture: nC6/3MP/22DMB	Molecular sieving	19
Co ₃ (HCOO) ₆	1D channels with 0.55 nm S_{BET} : 365 m ² .g ⁻¹	Adsorption equilibrium isotherms at 303 K - single component: nC6, 3MP, and 23DMB Multicomponent breakthrough curves at 303K - ternary mixture: nC6/3MP/22DMB	Molecular sieving	32
HIAM-302	Topology: lyu 1D channels S_{BET} : 388 m ² .g ⁻¹	Adsorption equilibrium isotherms at 303 K - single component: nC6, 3MP, and 23DMB Multicomponent breakthrough curves at 303 K and 353 K - ternary mixture: nC6/3MP/22DMB	Molecular sieving	33

A.2 References

- (1) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A Microporous Metal-Organic Framework for Gas-Chromatographic Separation of Alkanes. *Angew. Chemie - Int. Ed.* **2006**, *45*, 1390–1393.
- (2) Bárcia, P. S.; Zapata, F.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. Kinetic Separation of Hexane Isomers by Fixed-Bed Adsorption with a Microporous Metal-Organic Framework. *J. Phys. Chem. B* **2007**, *111*, 6101–6103.
- (3) Finsy, V.; Calero, S.; García-Pérez, E.; Merklings, P. J.; Vedts, G.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Low-Coverage Adsorption Properties of the Metal-Organic Framework MIL-47 Studied by Pulse Chromatography and Monte Carlo Simulations. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3515–3521.
- (4) Couck, S.; Rémy, T.; Baron, G. V.; Gascon, J.; Kapteijn, F.; Denayer, J. F. M. A Pulse Chromatographic Study of the Adsorption Properties of the Amino-MIL-53 (Al) Metal-Organic Framework. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9413–9418.
- (5) Ling, Y.; Chen, Z. X.; Zhai, F. P.; Zhou, Y. M.; Weng, L. H.; Zhao, D. Y. A Zinc(II) Metal-Organic Framework Based on Triazole and Dicarboxylate Ligands for Selective Adsorption of Hexane Isomers. *Chem. Commun.* **2011**, *47*, 7197–7199.
- (6) Bárcia, P. S.; Guimarães, D.; Mendes, P. A. P.; Silva, J. A. C.; Guillerm, V.; Chevreau, H.; Serre, C.; Rodrigues, A. E. Reverse Shape Selectivity in the Adsorption of Hexane and Xylene Isomers in MOF UiO-66. *Microporous Mesoporous Mater.* **2011**, *139*, 67–73.
- (7) Mendes, P. A. P.; Ragon, F.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Hexane Isomers Sorption on a Functionalized Metal-Organic Framework. *Microporous Mesoporous Mater.* **2013**, *170*, 251–258.
- (8) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. Separation of C6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A. *Ind. Eng. Chem. Res.* **2012**, *51*, 4692–4702.
- (9) Fan, L.; Yan, X. P. Evaluation of Isostructural Metal-Organic Frameworks Coated Capillary Columns for the Gas Chromatographic Separation of Alkane Isomers. *Talanta*

2012, 99, 944–950.

- (10) Mendes, P.; Rodrigues, A.; Horcajada, P.; Eubank, J.; Devic, T.; Serre, C.; Silva, J. Separation of Hexane Isomers on Rigid Porous Metal Carboxylate-Based Metal-Organic Frameworks. *Adsorpt. Sci. Technol.* **2014**, 32, 475–488.
- (11) Fang, Z. L.; Zheng, S. R.; Tan, J. B.; Cai, S. L.; Fan, J.; Yan, X.; Zhang, W. G. Tubular Metal-Organic Framework-Based Capillary Gas Chromatography Column for Separation of Alkanes and Aromatic Positional Isomers. *J. Chromatogr. A* **2013**, 1285, 132–138.
- (12) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; Van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels. *Science* **2013**, 340, 960–964.
- (13) Bozbiyik, B.; Lannoeye, J.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Shape Selective Properties of the Al-Fumarate Metal-Organic Framework in the Adsorption and Separation of n-Alkanes, Iso-Alkanes, Cyclo-Alkanes and Aromatic Hydrocarbons. *Phys. Chem. Chem. Phys.* **2016**, 18, 3294–3301.
- (14) Belarbi, H.; Boudjema, L.; Shepherd, C.; Ramsahye, N.; Toquer, G.; Chang, J. S.; Trens, P. Adsorption and Separation of Hydrocarbons by the Metal Organic Framework MIL-101(Cr). *Colloids Surfaces A Physicochem. Eng. Asp.* **2017**, 520, 46–52.
- (15) Wee, L. H.; Meledina, M.; Turner, S.; Van Tendeloo, G.; Zhang, K.; Rodriguez-Abelo, L. M.; Masala, A.; Bordiga, S.; Jiang, J.; Navarro, J. A. R.; Kirschhock, C. E. A.; Martens, J. A. 1D-2D-3D Transformation Synthesis of Hierarchical Metal-Organic Framework Adsorbent for Multicomponent Alkane Separation. *J. Am. Chem. Soc.* **2017**, 139, 819–828.
- (16) Wang, H.; Dong, X.; Lin, J.; Teat, S. J.; Jensen, S.; Cure, J.; Alexandrov, E. V.; Xia, Q.; Tan, K.; Wang, Q.; Olson, D. H.; Proserpio, D. M.; Chabal, Y. J.; Thonhauser, T.; Sun, J.; Han, Y.; Li, J. Topologically Guided Tuning of Zr-MOF Pore Structures for Highly Selective Separation of C6 Alkane Isomers. *Nat. Commun.* **2018**, 9, 1745.
- (17) Bury, W.; Walczak, A. M.; Leszczyński, M. K.; Navarro, J. A. R. Rational Design of Noncovalent Diamondoid Microporous Materials for Low-Energy Separation of C6-Hydrocarbons. *J. Am. Chem. Soc.* **2018**, 140, 15031–15037.

- (18) Wang, D.; Dong, X.; Han, Y.; Liu, Y. Separation of Hexane Isomers by Introducing “Triangular-like and Quadrilateral-like Channels” in a Bcu-Type Metal-Organic Framework. *Nano Res.* **2021**, *14*, 526–531.
- (19) Yu, Q.; Guo, L.; Lai, D.; Zhang, Z.; Yang, Q.; Yang, Y.; Ren, Q.; Bao, Z. A Pore-Engineered Metal-Organic Framework with Mixed Ligands Enabling Highly Efficient Separation of Hexane Isomers for Gasoline Upgrading. *Sep. Purif. Technol.* **2021**, *268*, 118646.
- (20) Vismara, R.; Di Nicola, C.; Millán, R. G. S.; Domasevich, K. V.; Pettinari, C.; Navarro, J. A. R.; Galli, S. Efficient Hexane Isomers Separation in Isorecticular Bipyrazolate Metal-Organic Frameworks: The Role of Pore Functionalization. *Nano Res.* **2021**, *14*, 532–540.
- (21) Chang, N.; Gu, Z. Y.; Yan, X. P. Zeolitic Imidazolate Framework-8 Nanocrystal Coated Capillary for Molecular Sieving of Branched Alkanes From Linear Alkanes along with High-Resolution Chromatographic Separation of Linear Alkanes. *J. Am. Chem. Soc.* **2010**, *132*, 13645–13647.
- (22) Mendes, P. A. P.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Single and Multicomponent Adsorption of Hexane Isomers in the Microporous ZIF-8. *Microporous Mesoporous Mater.* **2014**, *194*, 146–156.
- (23) Zhang, L.; Qian, G.; Liu, Z.; Cui, Q.; Wang, H.; Yao, H. Adsorption and Separation Properties of N-Pentane/Isopentane on ZIF-8. *Sep. Purif. Technol.* **2015**, *156*, 472–479.
- (24) Ferreira, A. F. P.; Mittelmeijer-Hazeleger, M. C.; Granato, M. A.; Martins, V. F. D.; Rodrigues, A. E.; Rothenberg, G. Sieving Di-Branched from Mono-Branched and Linear Alkanes Using ZIF-8: Experimental Proof and Theoretical Explanation. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8795–8804.
- (25) Zhang, K.; Lively, R. P.; Zhang, C.; Chance, R. R.; Koros, W. J.; Sholl, D. S.; Nair, S. Exploring the Framework Hydrophobicity and Flexibility of Zif-8: From Biofuel Recovery to Hydrocarbon Separations. *J. Phys. Chem. Lett.* **2013**, *4*, 3618–3622.
- (26) Mendes, P. A. P.; Horcajada, P.; Rives, S.; Ren, H.; Rodrigues, A. E.; Devic, T.; Magnier, E.; Trens, P.; Jobic, H.; Ollivier, J.; Maurin, G.; Serre, C.; Silva, J. A. C. A Complete Separation of Hexane Isomers by a Functionalized Flexible Metal Organic

Framework. *Adv. Funct. Mater.* **2014**, *24*, 7666–7673.

- (27) Lv, D.; Wang, H.; Chen, Y.; Xu, F.; Shi, R.; Liu, Z.; Wang, X.; Teat, S. J.; Xia, Q.; Li, Z.; Li, J. Iron-Based Metal-Organic Framework with Hydrophobic Quadrilateral Channels for Highly Selective Separation of Hexane Isomers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 6031–6038.
- (28) Velasco, E.; Xian, S.; Wang, H.; Teat, S. J.; Olson, D. H.; Tan, K.; Ullah, S.; Osborn Popp, T. M.; Bernstein, A. D.; Oyekan, K. A.; Nieuwkoop, A. J.; Thonhauser, T.; Li, J. Flexible Zn-MOF with Rare Underlying Scu Topology for Effective Separation of C6 Alkane Isomers. *ACS Appl. Mater. Interfaces* **2021**, *13*, 51997–52005.
- (29) Assen, A. H.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Xue, D. X.; Jiang, H.; Eddaoudi, M. Ultra-Tuning of the Rare-Earth Fcu-MOF Aperture Size for Selective Molecular Exclusion of Branched Paraffins. *Angew. Chemie - Int. Ed.* **2015**, *54*, 14353–14358.
- (30) Wang, H.; Dong, X.; Velasco, E.; Olson, D. H.; Han, Y.; Li, J. One-of-a-Kind: A Microporous Metal-Organic Framework Capable of Adsorptive Separation of Linear, Mono- and Di-Branched Alkane Isomers via Temperature- and Adsorbate-Dependent Molecular Sieving. *Energy Environ. Sci.* **2018**, *11*, 1226–1231.
- (31) Yu, L.; Dong, X.; Gong, Q.; Acharya, S. R.; Lin, Y.; Wang, H.; Han, Y.; Thonhauser, T.; Li, J. Splitting Mono- and Dibranched Alkane Isomers by a Robust Aluminum-Based Metal-Organic Framework Material with Optimal Pore Dimensions. *J. Am. Chem. Soc.* **2020**, *142*, 6925–6929.
- (32) Wang, H.; Dong, X.; Ding, J.; Wang, K.; Yu, L.; Zhang, S.; Han, Y.; Gong, Q.; Ma, A.; Li, J. Upgrading Octane Number of Naphtha by a Robust and Easily Attainable Metal-Organic Framework through Selective Molecular Sieving of Alkane Isomers. *Chem. - A Eur. J.* **2021**, *27*, 11795–11798.
- (33) Yu, L.; Ullah, S.; Zhou, K.; Xia, Q.; Wang, H.; Tu, S.; Huang, J.; Xia, H. L.; Liu, X. Y.; Thonhauser, T.; Li, J. A Microporous Metal-Organic Framework Incorporating Both Primary and Secondary Building Units for Splitting Alkane Isomers. *J. Am. Chem. Soc.* **2022**, *144*, 3766–3770.

Appendix B

B.1 Single Component Adsorption of nC5 and nC6 Alkanes in ZIF-8

Figures B.1 and B.2 show the single component breakthrough curves of nC5 and nC6 alkanes in ZIF-8 at the alkane partial pressures of a) 5 kPa, b) 10 kPa, c) 25 kPa, d) 37 kPa, and e) 50 kPa. In each panel, the effect of the temperature is shown. The mean retention time for each component, t_{rt} (s), calculated from a mass balance over the column (Eq. B.1)¹, is also given in the figures:

$$t_{rt} = \left(\frac{L\varepsilon_b}{v_{sup}} \right) \left(1 + \frac{\rho_b q}{\varepsilon_b C_f} \right) \quad (\text{B.1})$$

One can observe for both components, especially at the lowest temperature of 373 K, an apparent change in the shape of the breakthrough concentration profiles with increasing the alkane partial pressure (high feed concentration). The breakthroughs become steeper due to the favourable nature of the adsorption isotherm (approaching a rectangular form (see Figure 4.5)). At the highest temperature of 473 K, the breakthroughs spread along the time axis, becoming more dispersed (wide mass transfer zone). This is because the isotherm approaches a linear shape at this temperature, in which the adsorption dynamics are dominated by mass transfer resistances and axial dispersion in the bed.

The effect of the alkane partial pressure over the t_{rt} is also evidenced in Figures B1 and B2. For instance, considering the linear nC5 for the same temperature of 373 K, when its feed concentration is lower, a longer time is required to reach the saturation of the adsorption column, being approximately 136 min at 11.1 kPa compared to 48 min at 53.0 kPa. This can be explained from Eq. B.1 where the ratio q/C_f decreases with increasing concentration in an isotherm approaching a rectangular form since q is practically constant, and consequently t_{rt} reduces. Finally, for the same feed concentration, the values of t_{rt} are substantially lower for

both alkanes at higher temperatures, reflecting the strong impact of this variable on their adsorption behaviour.

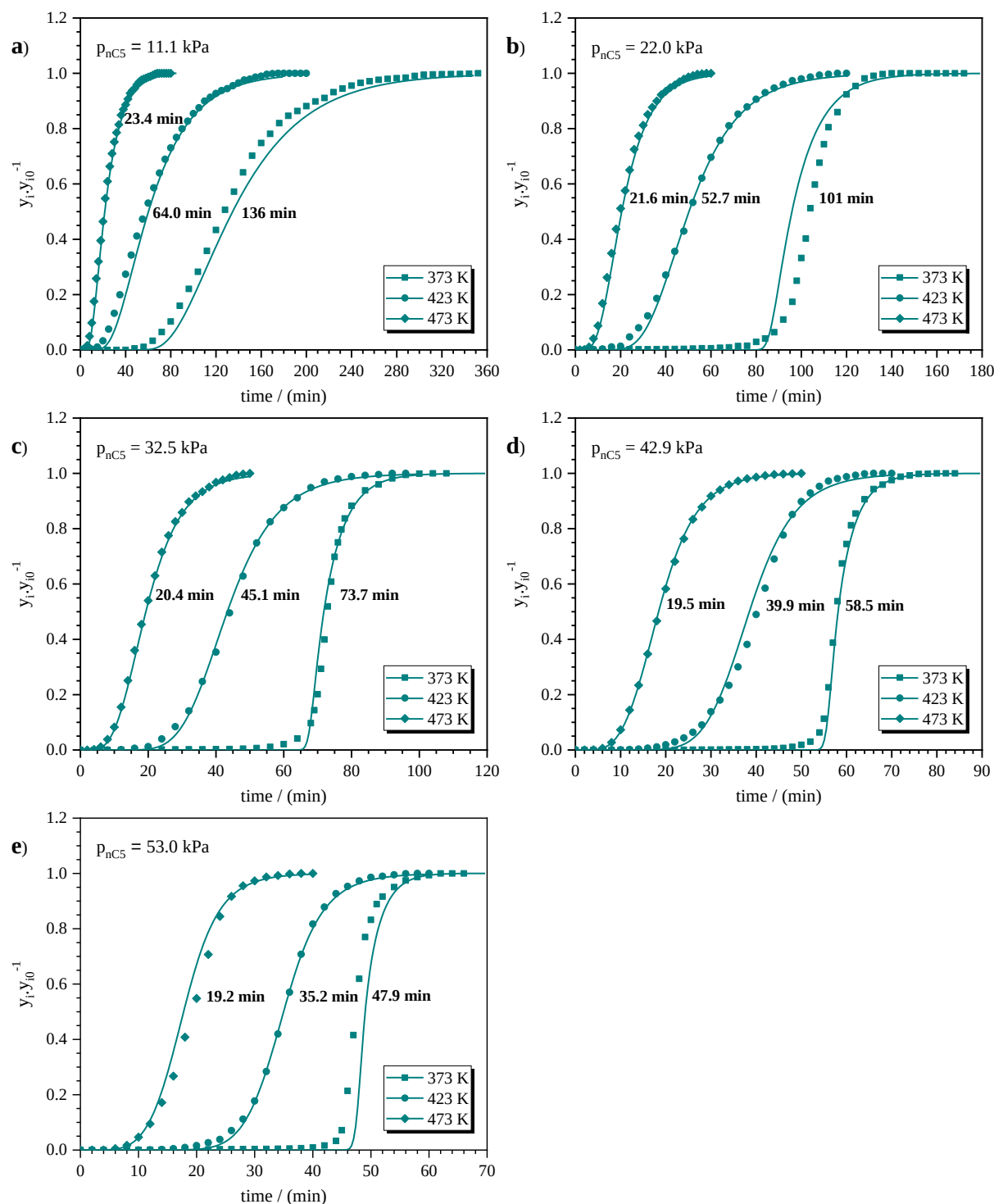


Figure B.1 | Experimental and numerical single component breakthrough curves of nC5 in ZIF-8 at the temperature range of 373 - 473 K: a) 11.1 kPa, b) 42.9 kPa, c) 22.0 kPa, d) 32.5 kPa, and e) 53.0 kPa. The continuous lines represent the numerical simulations.

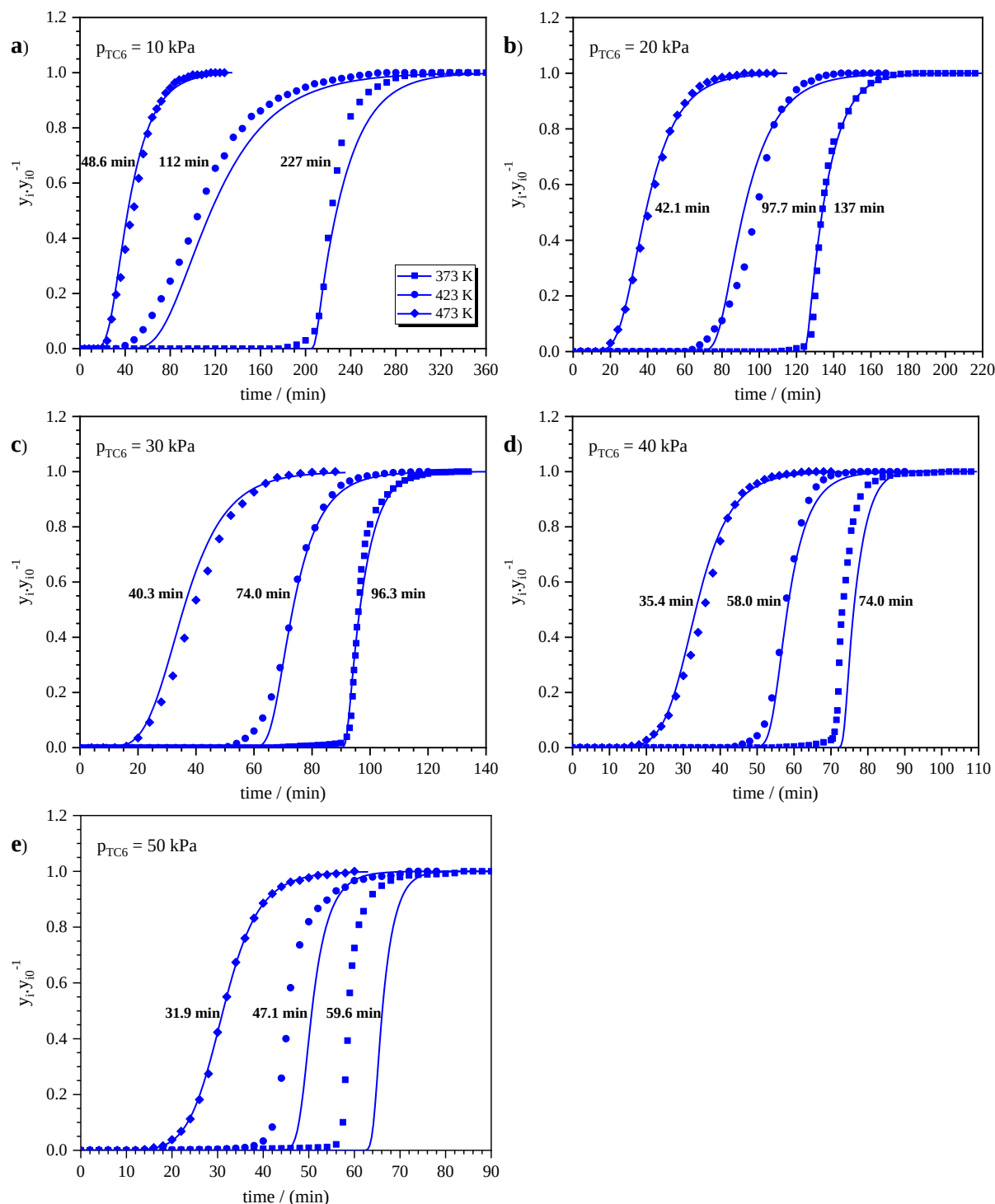


Figure B.2 | Experimental and numerical single component breakthrough curves of nC6 in ZIF-8 at the temperature range of 373 - 473 K: a) 10 kPa, b) 20 kPa, c) 30 kPa, d) 40 kPa, and e) 50 kPa. The continuous lines represent the numerical simulations.

Regarding the numerical simulations represented by the continuous lines in the figures, a good agreement between the mathematical model predictions and experimental data is observed. The shapes of the breakthrough curves and the width of the mass transfer zone were qualitatively well described in most cases. The corresponding model parameters used in the

simulations are summarised in Tables B.1 - B.3 and B.4 - B.6 for the nC5 and nC6 alkanes, respectively.

Table B.1 | Model parameters for simulating the single component breakthrough curves of nC5 in ZIF-8 at 373 K.

T	(K)	3.73×10^2	3.73×10^2	3.73×10^2	3.73×10^2	3.73×10^2
p_{nC5}	(kPa)	1.11×10^1	2.20×10^1	3.25×10^1	4.29×10^1	5.30×10^1
C_t	(mol.m ⁻³)	3.22×10^1	3.22×10^1	3.22×10^1	3.22×10^1	3.22×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.46×10^1	4.81×10^1	6.12×10^1	7.41×10^1	8.66×10^1
D_{ax}	(m ² .s ⁻¹)	3.51×10^{-5}	3.52×10^{-5}	3.52×10^{-5}	3.52×10^{-5}	3.52×10^{-5}
D_{mnc5}	(m ² .s ⁻¹)	4.87×10^{-5}	4.87×10^{-5}	4.87×10^{-5}	4.87×10^{-5}	4.87×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	1.16×10^2	8.38×10^1	6.58×10^1	5.43×10^1	4.62×10^1
h_w	(W.m ⁻² .K ⁻¹)	6.20×10^0	1.24×10^1	1.59×10^1	1.95×10^1	2.31×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.50×10^{-1}	2.99×10^{-1}	2.65×10^{-1}	2.40×10^{-1}	2.21×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.08×10^{-1}	7.58×10^{-2}	5.77×10^{-2}	4.61×10^{-2}	3.80×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.69×10^{-5}	1.39×10^{-5}	1.23×10^{-5}	1.12×10^{-5}	1.04×10^{-5}
v_{int}	(m.s ⁻¹)	2.67×10^{-3}	2.73×10^{-3}	2.77×10^{-3}	2.80×10^{-3}	2.83×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.80×10^2	1.91×10^2	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.2 | Model parameters for simulating the single component breakthrough curves of nC5 in ZIF-8 at 423 K.

T	(K)	4.23×10^2	4.23×10^2	4.23×10^2	4.23×10^2	4.23×10^2
p_{nC5}	(kPa)	1.11×10^1	2.20×10^1	3.25×10^1	4.29×10^1	5.30×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.84×10^1	2.84×10^1	2.84×10^1	2.84×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.63×10^1	5.15×10^1	6.62×10^1	8.07×10^1	9.47×10^1
D_{ax}	(m ² .s ⁻¹)	4.33×10^{-5}	4.33×10^{-5}	4.34×10^{-5}	4.34×10^{-5}	4.34×10^{-5}
D_{mnc5}	(m ² .s ⁻¹)	6.01×10^{-5}	6.01×10^{-5}	6.01×10^{-5}	6.01×10^{-5}	6.01×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	128×10^2	9.42×10^1	7.48×10^1	6.23×10^1	5.35×10^1
h_w	(W.m ⁻² .K ⁻¹)	9.11×10^0	1.32×10^1	1.72×10^1	2.12×10^1	2.52×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.70×10^{-1}	3.19×10^{-1}	2.84×10^{-1}	2.59×10^{-1}	2.40×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.20×10^{-1}	8.56×10^{-2}	6.60×10^{-2}	5.33×10^{-2}	4.45×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.87×10^{-5}	1.55×10^{-5}	1.37×10^{-5}	1.26×10^{-5}	1.17×10^{-5}
v_{int}	(m.s ⁻¹)	3.02×10^{-3}	3.10×10^{-3}	3.14×10^{-3}	3.18×10^{-3}	3.21×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.3 | Model parameters for simulating the single component breakthrough curves of nC5 in ZIF-8 at 473 K.

T	(K)	4.73×10^2	4.73×10^2	4.73×10^2	4.73×10^2	4.73×10^2
p_{nC5}	(kPa)	1.11×10^1	2.20×10^1	3.25×10^1	4.29×10^1	5.30×10^1
C_t	(mol.m ⁻³)	2.54×10^1	2.54×10^1	2.54×10^1	2.54×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.79×10^1	5.46×10^1	7.09×10^1	8.68×10^1	1.02×10^2
D_{ax}	(m ² .s ⁻¹)	5.21×10^{-5}	5.22×10^{-5}	5.22×10^{-5}	5.22×10^{-5}	5.22×10^{-5}
D_{mnc5}	(m ² .s ⁻¹)	7.25×10^{-5}	7.25×10^{-5}	7.25×10^{-5}	7.25×10^{-5}	7.25×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	1.40×10^2	1.04×10^2	8.38×10^1	7.04×10^1	6.10×10^1
h_w	(W.m ⁻² .K ⁻¹)	9.51×10^0	1.40×10^1	1.84×10^1	2.29×10^1	2.73×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.86×10^{-1}	3.35×10^{-1}	3.01×10^{-1}	2.75×10^{-1}	2.57×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.32×10^{-1}	9.53×10^{-2}	7.42×10^{-2}	6.06×10^{-2}	5.10×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	2.04×10^{-5}	1.71×10^{-5}	1.52×10^{-5}	1.39×10^{-5}	1.30×10^{-5}
v_{int}	(m.s ⁻¹)	3.38×10^{-3}	3.47×10^{-3}	3.51×10^{-3}	3.55×10^{-3}	3.59×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.4 | Model parameters for simulating the single component breakthrough curves of nC6 in ZIF-8 at 373 K.

T	(K)	3.73×10^2	3.73×10^2	3.73×10^2	3.73×10^2	3.73×10^2
p_{nC6}	(kPa)	1.00×10^1	2.00×10^1	3.00×10^1	4.00×10^1	5.00×10^1
C_t	(mol.m ⁻³)	3.22×10^1	3.22×10^1	3.22×10^1	3.22×10^1	3.22×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.60×10^1	5.12×10^1	6.64×10^1	8.16×10^1	9.68×10^2
D_{ax}	(m ² .s ⁻¹)	3.36×10^{-5}	3.36×10^{-5}	3.36×10^{-5}	3.36×10^{-5}	3.36×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	4.64×10^{-5}	4.64×10^{-5}	4.64×10^{-5}	4.64×10^{-5}	4.64×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	1.16×10^2	8.35×10^1	5.37×10^1	5.37×10^1	4.55×10^1
h_w	(W.m ⁻² .K ⁻¹)	1.03×10^1	1.47×10^1	1.90×10^1	2.34×10^1	2.77×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.50×10^{-1}	2.99×10^{-1}	2.66×10^{-1}	2.40×10^{-1}	2.21×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.08×10^{-1}	7.54×10^{-2}	5.71×10^{-2}	4.53×10^{-2}	3.71×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.67×10^{-5}	1.37×10^{-5}	1.20×10^{-5}	1.09×10^{-5}	1.01×10^{-5}
v_{int}	(m.s ⁻¹)	2.67×10^{-3}	2.67×10^{-3}	2.67×10^{-3}	2.67×10^{-3}	2.67×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.80×10^2	1.80×10^2	1.80×10^2	1.80×10^2	1.80×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.5 | Model parameters for simulating the single component breakthrough curves of nC6 in ZIF-8 at 423 K.

T	(K)	4.23×10^2	4.23×10^2	4.23×10^2	4.23×10^2	4.23×10^2
p_{nC6}	(kPa)	1.00×10^1	2.00×10^1	3.00×10^1	4.00×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.84×10^1	2.84×10^1	2.84×10^1	2.84×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.78×10^1	5.48×10^1	7.18×10^1	8.89×10^1	1.06×10^2
D_{ax}	(m ² .s ⁻¹)	4.14×10^{-5}	4.14×10^{-5}	4.14×10^{-5}	4.14×10^{-5}	4.14×10^{-5}
D_{mnc6}	(m ² .s ⁻¹)	5.74×10^{-5}	5.74×10^{-5}	5.74×10^{-5}	5.74×10^{-5}	5.74×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	1.28×10^2	9.41×10^1	7.45×10^1	6.18×10^1	5.29×10^1
h_w	(W.m ⁻² .K ⁻¹)	9.48×10^0	1.37×10^1	1.80×10^1	2.23×10^1	2.65×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.71×10^{-1}	3.19×10^{-1}	2.84×10^{-1}	2.58×10^{-1}	2.39×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.20×10^{-1}	8.53×10^{-2}	6.54×10^{-2}	5.26×10^{-2}	4.36×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.85×10^{-5}	1.53×10^{-5}	1.35×10^{-5}	1.23×10^{-5}	1.14×10^{-5}
v_{int}	(m.s ⁻¹)	3.02×10^{-3}	3.02×10^{-3}	3.02×10^{-3}	3.02×10^{-3}	3.02×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.80×10^2	1.91×10^2	1.91×10^2	1.80×10^2	1.80×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.6 | Model parameters for simulating the single component breakthrough curves of nC6 in ZIF-8 at 473 K.

T	(K)	4.73 x 10 ²	4.73 x 10 ²	4.73 x 10 ²	4.73 x 10 ²	4.73 x 10 ²
p_{nC6}	(kPa)	1.00 x 10 ¹	2.00 x 10 ¹	3.00 x 10 ¹	4.00 x 10 ¹	5.00 x 10 ¹
C_t	(mol.m ⁻³)	2.54 x 10 ¹	2.54 x 10 ¹	2.54 x 10 ¹	2.54 x 10 ¹	2.54 x 10 ¹
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.95 x 10 ¹	5.82 x 10 ¹	7.70 x 10 ¹	9.57 x 10 ¹	1.14 x 10 ²
D_{ax}	(m ² .s ⁻¹)	4.99 x 10 ⁻⁵	4.99 x 10 ⁻⁵	4.99 x 10 ⁻⁵	4.99 x 10 ⁻⁵	4.99 x 10 ⁻⁵
D_{mnC6}	(m ² .s ⁻¹)	6.93 x 10 ⁻⁵	6.93 x 10 ⁻⁵	6.93 x 10 ⁻⁵	6.93 x 10 ⁻⁵	6.93 x 10 ⁻⁵
h_f	(W.m ⁻² .K ⁻¹)	1.41 x 10 ²	1.05 x 10 ²	8.36 x 10 ¹	7.00 x 10 ¹	6.04 x 10 ¹
h_w	(W.m ⁻² .K ⁻¹)	9.91 x 10 ⁰	1.46 x 10 ¹	1.93 x 10 ¹	2.40 x 10 ¹	2.87 x 10 ¹
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.86 x 10 ⁻¹	3.35 x 10 ⁻¹	3.00 x 10 ⁻¹	2.74 x 10 ⁻¹	2.56 x 10 ⁻¹
k_g	(W.m ⁻¹ .K ⁻¹)	1.32 x 10 ⁻¹	9.15 x 10 ⁻²	7.38 x 10 ⁻²	5.99 x 10 ⁻²	5.02 x 10 ⁻²
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73 x 10 ⁻¹	1.73 x 10 ⁻¹	1.73 x 10 ⁻¹	1.73 x 10 ⁻¹	1.73 x 10 ⁻¹
μ_g	(Pa.s)	2.03 x 10 ⁻⁵	1.69 x 10 ⁻⁵	1.49 x 10 ⁻⁵	1.36 x 10 ⁻⁵	1.27 x 10 ⁻⁵
v_{int}	(m.s ⁻¹)	3.38 x 10 ⁻³	3.38 x 10 ⁻³	3.38 x 10 ⁻³	3.38 x 10 ⁻³	3.38 x 10 ⁻³
a_c	(m ⁻¹)	4.00 x 10 ²	4.00 x 10 ²	4.00 x 10 ²	4.00 x 10 ²	4.00 x 10 ²
a_p	(m ⁻¹)	3.00 x 10 ³	3.00 x 10 ³	3.00 x 10 ³	3.00 x 10 ³	3.00 x 10 ³
ρ_b	(kg.m ⁻³)	1.91 x 10 ²	1.91 x 10 ²	1.91 x 10 ²	1.91 x 10 ²	1.91 x 10 ²
d_p	(m)	2.00 x 10 ⁻³	2.00 x 10 ⁻³	2.00 x 10 ⁻³	2.00 x 10 ⁻³	2.00 x 10 ⁻³
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60 x 10 ³	1.60 x 10 ³	1.60 x 10 ³	1.60 x 10 ³	1.60 x 10 ³
ε_b	(-)	4.00 x 10 ⁻¹	4.00 x 10 ⁻¹	4.00 x 10 ⁻¹	4.00 x 10 ⁻¹	4.00 x 10 ⁻¹

B.2 Multicomponent Adsorption of Pentane and Hexane Isomers in ZIF-8

Figure B.3 shows the numerical simulations for the breakthrough curves in which it was assumed weak diffusional resistances and equal for all the pentane and hexane isomers ($k_{LDF,nC6} = k_{LDF,nC5} = 0.0643 \text{ s}^{-1}$), being the ratios $k_{LDF,nC6}/k_{LDF,iC5}$, $k_{LDF,nC6}/k_{LDF,2MP}$, $k_{LDF,nC6}/k_{LDF,3MP}$, $k_{LDF,nC6}/k_{LDF,23DMB}$, and $k_{LDF,nC6}/k_{LDF,22DMB}$ equal to 1. In the figure, a simulation for each multicomponent system addressed in *Chapter 4* is shown: a) quinary equimolar mixture of hexane isomers, b) septenary equimolar mixture of pentane and hexane isomers, and c) quinary equimolar mixture of pentane and hexane branched alkanes.

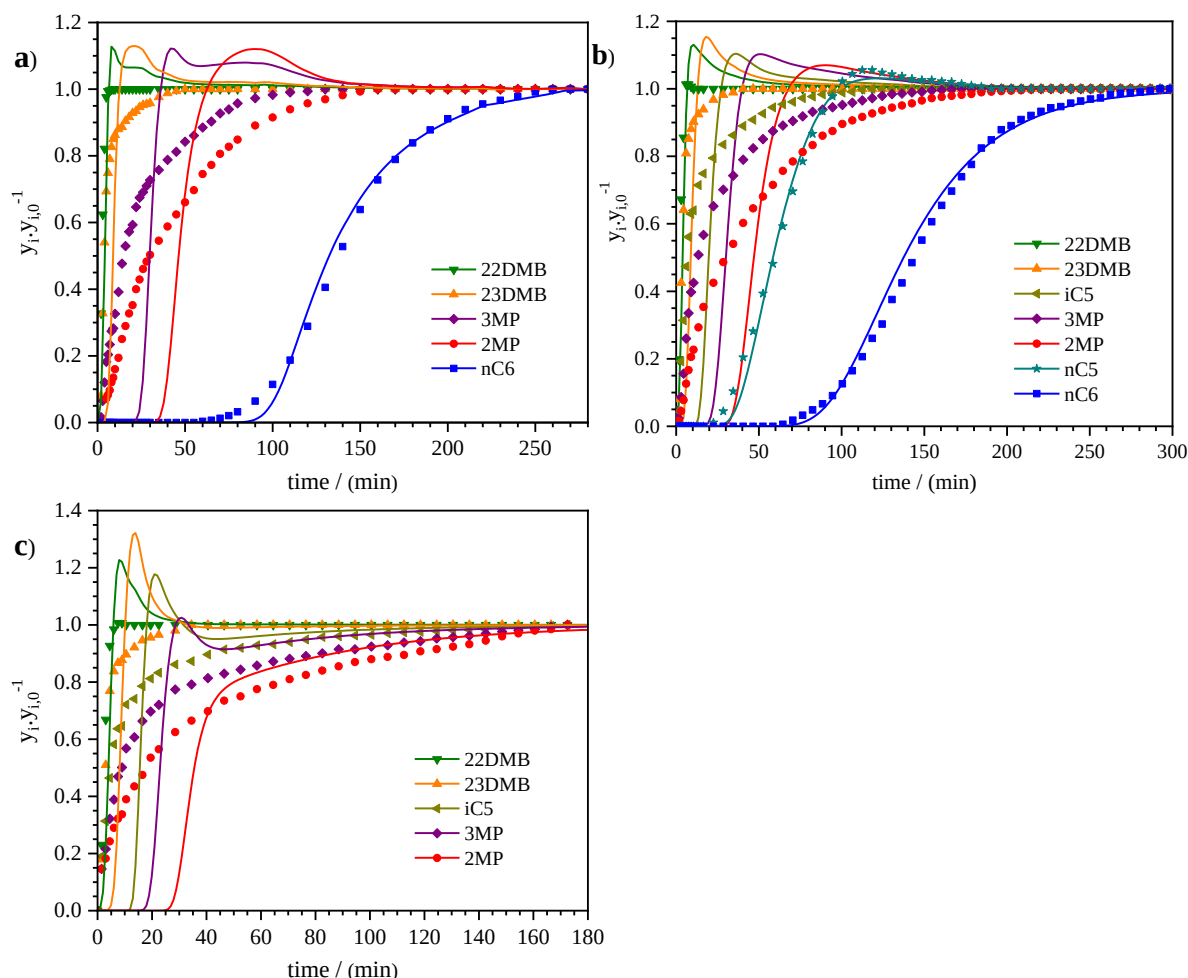


Figure B.3 | Experimental and numerical breakthrough curves for equimolar mixtures of pentane and hexane isomers in ZIF-8 at 423 K and 25 kPa: a) quinary mixture of hexane isomers, b) septenary mixture of pentane and hexane isomers, and c) quinary mixture of pentane and hexane branched alkanes. The continuous lines represent the numerical simulations. These simulations accounts for weak diffusional resistances and equal for all alkanes with $k_{LDF} = 0.0643 \text{ s}^{-1}$.

As demonstrated, completely different behaviour was observed compared to the simulations highlighted in *Chapter 4*, showing that it was only possible to qualitatively represent the experimental data by accounting for strong diffusional resistances for the branched alkanes, according to the values reported in Table 4.7. These observations prove that the sorption of branched paraffins in ZIF-8 is strongly diffusional limited in contrast with the linear ones, which are essentially equilibrium-based.

Tables B.7 – B.10, B.11, and B.12 summarise the model parameters used in the numerical simulations of the breakthrough curves for a quinary equimolar mixture of hexane isomers, septenary equimolar mixture of pentane and hexane isomers, and septenary equimolar mixture of pentane and hexane branched alkanes in ZIF-8, respectively.

Table B.7 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 373 K.

T	(K)	3.73×10^2	3.73×10^2	3.73×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	3.22×10^1	3.22×10^1	3.22×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.60×10^1	5.88×10^1	9.69×10^1
D_{ax}	(m ² .s ⁻¹)	1.63×10^{-5}	9.39×10^{-6}	5.62×10^{-6}
D_{mnC6}	(m ² .s ⁻¹)	2.18×10^{-5}	1.19×10^{-5}	6.51×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	1.67×10^{-5}	9.66×10^{-6}	5.48×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.55×10^{-5}	9.09×10^{-6}	5.19×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	1.91×10^{-5}	1.06×10^{-5}	5.89×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	1.78×10^{-5}	1.02×10^{-5}	5.75×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	1.02×10^2	6.07×10^1	3.64×10^1
h_w	(W.m ⁻² .K ⁻¹)	3.87×10^0	2.53×10^1	4.16×10^1
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.30×10^{-1}	2.50×10^{-1}	2.00×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	9.00×10^{-2}	5.00×10^{-2}	3.00×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.43×10^{-5}	1.01×10^{-5}	7.64×10^{-6}
v_{int}	(m.s ⁻¹)	2.67×10^{-3}	2.67×10^{-3}	2.67×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.8 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 423 K.

T	(K)	4.23×10^2	4.23×10^2	4.23×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.84×10^1	2.84×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.79×10^1	6.35×10^1	1.06×10^2
D_{ax}	(m ² .s ⁻¹)	2.05×10^{-5}	1.18×10^{-5}	7.02×10^{-6}
D_{mnC6}	(m ² .s ⁻¹)	2.75×10^{-5}	1.51×10^{-5}	8.31×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	2.09×10^{-5}	1.22×10^{-5}	6.96×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.95×10^{-5}	1.15×10^{-6}	6.60×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	2.45×10^{-5}	1.35×10^{-5}	7.52×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	2.24×10^{-5}	1.29×10^{-5}	7.31×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	1.13×10^2	6.85×10^1	4.20×10^1
h_w	(W.m ⁻² .K ⁻¹)	1.36×10^0	3.18×10^0	5.32×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.50×10^{-1}	2.70×10^{-1}	2.10×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.10×10^{-1}	6.00×10^{-2}	3.00×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.28×10^{-5}	1.13×10^{-5}	8.59×10^{-6}
v_{int}	(m.s ⁻¹)	3.02×10^{-3}	3.02×10^{-3}	3.02×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.9 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in ZIF-8 at 473 K.

T	(K)	4.73×10^2	4.73×10^2	4.73×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.54×10^1	2.54×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.96×10^1	6.79×10^1	1.15×10^2
D_{ax}	(m ² .s ⁻¹)	2.50×10^{-5}	1.44×10^{-5}	8.56×10^{-6}
D_{mnC6}	(m ² .s ⁻¹)	3.38×10^{-5}	1.86×10^{-5}	1.03×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	2.56×10^{-5}	1.50×10^{-5}	8.59×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	2.38×10^{-5}	1.41×10^{-5}	8.14×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	2.95×10^{-5}	1.67×10^{-5}	9.32×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	2.73×10^{-5}	1.59×10^{-5}	9.02×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	1.23×10^2	7.62×10^1	4.77×10^1
h_w	(W.m ⁻² .K ⁻¹)	2.55×10^0	4.37×10^0	7.41×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.60×10^{-1}	2.90×10^{-1}	2.30×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.20×10^{-1}	7.00×10^{-2}	4.00×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.73×10^{-5}	1.24×10^{-5}	9.50×10^{-6}
v_{int}	(m.s ⁻¹)	3.38×10^{-3}	3.38×10^{-3}	3.38×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.10 | Model parameters for simulating the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in ZIF-8 373, 423, and 473 K.

T	(K)	3.73×10^2	4.23×10^2	4.73×10^2
p_T	(kPa)	2.50×10^1	2.50×10^1	2.50×10^1
C_t	(mol.m ⁻³)	3.22×10^1	2.84×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	5.68×10^1	6.13×10^1	6.54×10^1
D_{ax}	(m ² .s ⁻¹)	9.70×10^{-6}	1.22×10^{-5}	1.49×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	1.34×10^{-5}	1.70×10^{-5}	2.10×10^{-5}
D_{miC5}	(m ² .s ⁻¹)	1.35×10^{-5}	1.71×10^{-5}	2.11×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	1.23×10^{-5}	1.57×10^{-5}	1.94×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	9.84×10^{-6}	1.24×10^{-5}	1.53×10^{-5}
D_{m3MP}	(m ² .s ⁻¹)	9.21×10^{-6}	1.17×10^{-5}	1.43×10^{-5}
D_{m23DMB}	(m ² .s ⁻¹)	1.09×10^{-5}	1.39×10^{-5}	1.71×10^{-5}
D_{m22DMB}	(m ² .s ⁻¹)	1.04×10^{-5}	1.32×10^{-5}	1.62×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	6.47×10^1	7.31×10^1	8.12×10^1
h_w	(W.m ⁻² .K ⁻¹)	8.14×10^0	4.39×10^0	4.69×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	2.63×10^{-1}	2.81×10^{-1}	2.96×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	5.70×10^{-2}	6.47×10^{-2}	7.23×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.09×10^{-5}	1.22×10^{-5}	1.34×10^{-5}
v_{int}	(m.s ⁻¹)	2.67×10^{-3}	3.02×10^{-3}	3.38×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table B.11 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of pentane and hexane branched alkanes in ZIF-8 at 373, 423, and 473 K.

T	(K)	3.73×10^2	4.23×10^2	4.73×10^2
p_T	(kPa)	2.50×10^1	2.50×10^1	2.50×10^1
C_t	(mol.m ⁻³)	3.22×10^1	2.84×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	5.74×10^1	6.20×10^1	6.62×10^1
D_{ax}	(m ² .s ⁻¹)	7.95×10^{-6}	9.91×10^{-6}	1.20×10^{-5}
D_{miC5}	(m ² .s ⁻¹)	1.32×10^{-5}	1.67×10^{-5}	2.05×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	9.83×10^{-6}	1.24×10^{-5}	1.53×10^{-5}
D_{m3MP}	(m ² .s ⁻¹)	9.25×10^{-6}	1.17×10^{-5}	1.44×10^{-5}
D_{m23DMB}	(m ² .s ⁻¹)	1.08×10^{-5}	1.38×10^{-5}	1.70×10^{-5}
D_{m22DMB}	(m ² .s ⁻¹)	1.04×10^{-5}	1.31×10^{-5}	1.61×10^{-5}
h_f	(W.m ⁻² .K ⁻¹)	6.13×10^1	6.91×10^1	7.67×10^1
h_w	(W.m ⁻² .K ⁻¹)	2.06×10^{-1}	4.44×10^{-1}	2.37×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	2.56×10^{-1}	2.73×10^{-1}	2.88×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	5.37×10^{-2}	6.08×10^{-2}	6.79×10^{-2}
k_s^2	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.02×10^{-5}	1.14×10^{-5}	1.25×10^{-5}
v_{int}	(m.s ⁻¹)	2.67×10^{-3}	3.02×10^{-3}	3.38×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	3.00×10^3	3.00×10^3	3.00×10^3
ρ_b	(kg.m ⁻³)	1.91×10^2	1.91×10^2	1.91×10^2
d_p	(m)	2.00×10^{-3}	2.00×10^{-3}	2.00×10^{-3}
c_{ps}^3	(J.kg ⁻¹ .K ⁻¹)	1.60×10^3	1.60×10^3	1.60×10^3
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

B.3 References

- (1) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons, 1984.
- (2) Zhang, X., Jiang, J. Thermal Conductivity of Zeolitic Imidazolate Framework-8: A molecular Simulation Study. *J. Phys. Chem. C* **2013**, *117*, 18441–18447.
- (3) Mendes, P. A. P.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. Single and

Multicomponent Adsorption of Hexane Isomers in the Microporous ZIF-8. *Microporous Mesoporous Mater.* **2014**, 194, 146–156.

Appendix C

C.1 Single Component Adsorption of Hexane Isomers in MIL-140B

Figures C.1, C.2, and C.3 give the single component breakthrough curves of hexane isomers in MIL-140B at the temperatures of 343, 373, and 423 K, respectively. In each figure, the effect of alkane partial pressure is shown: a) 5 kPa, b) 10 kPa, c) 25 kPa, d) 37 kPa, and e) 50 kPa. The mean retention time for each component (Eq. B.1, *Appendix B*) is also specified in the figures.

As demonstrated in Figure C.1, at 343 K, a clear tendency for separating the hexane isomers according to the degree of branching, linear (nC6) > mono-branched (2MP/3MP) > di-branched (23DMB/22DMB) is obtained, especially at low alkane partial pressures. For example, at 5.0 kPa, the differences between the mean residence time of the isomers are approximate: $t_{rt(nC6)} - t_{rt(2MP/3MP)} = 11$ min, $t_{rt(nC6)} - t_{rt(23DMB/22DMB)} = 19$ min, and $t_{rt(2MP/3MP)} - t_{rt(23DMB/22DMB)} = 9$ min. At the highest alkane partial pressure, 50 kPa, these values reduce to: $t_{rt(nC6)} - t_{rt(2MP/3MP)} = 2$ min, $t_{rt(nC6)} - t_{rt(23DMB/22DMB)} = 5$ min, and $t_{rt(2MP/3MP)} - t_{rt(23DMB/22DMB)} = 4.7$ min, but still, there is a favourable degree of separation of linear and mono-branched isomers from the di-branched ones (nC6/2MP/3MP > 23DMB/22DMB). However, this separation between LRON and HRON hexanes is strongly affected when the temperature increases. At 423 K (Figure C.3), the breakthrough curves of branched components tend to be closer, and the separation between mono from di-branched isomers becomes negligible, where the differences between their residence times are no longer than 1 min.

Finally, from an overall perspective, for each temperature, there is practically no change in the shape of the breakthrough concentration profiles of hexane isomers with increasing

alkane partial pressure. This suggests that the width of the mass transfer zone is similar in the entire range of working conditions addressed.

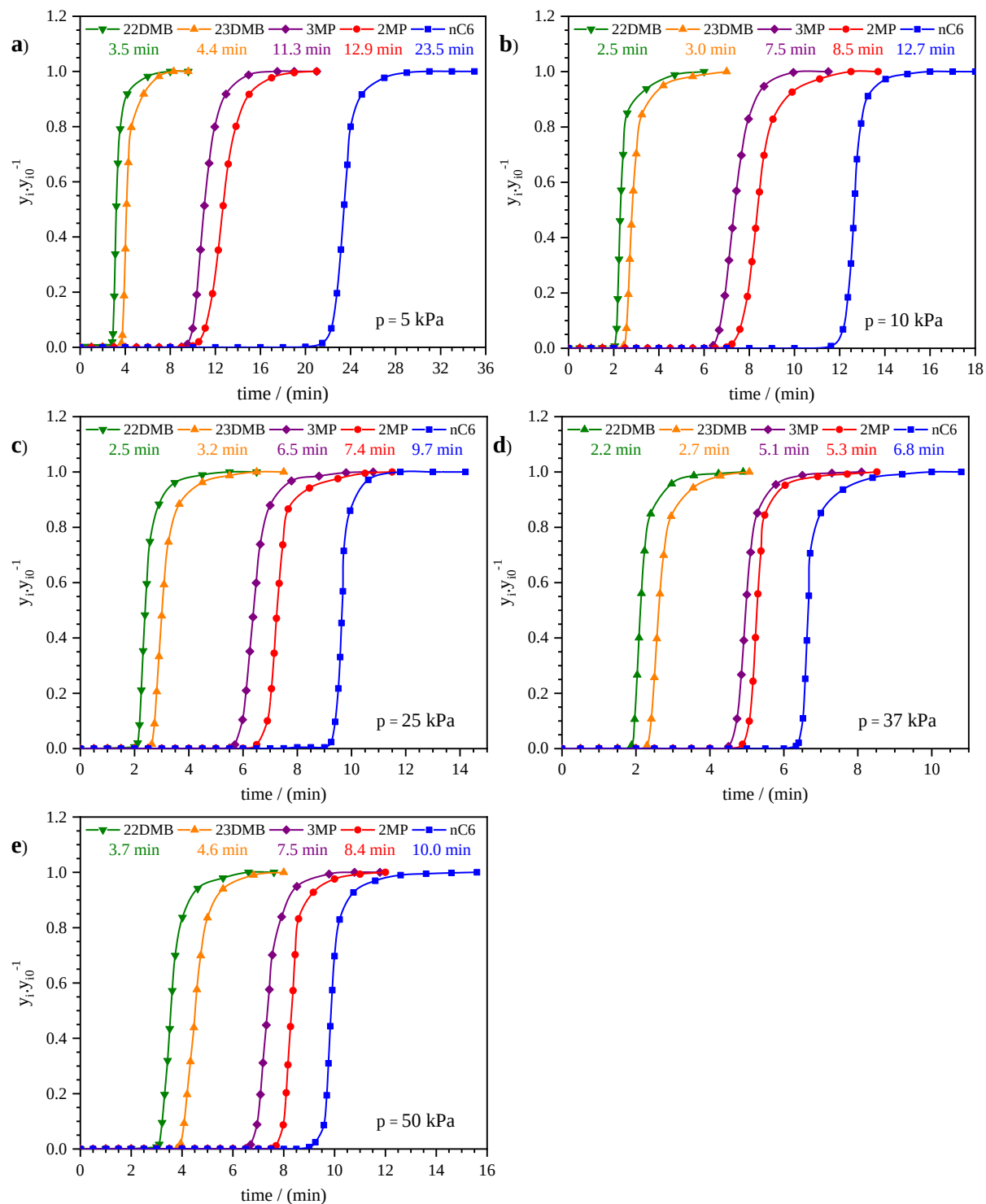


Figure C.1 | Experimental single component breakthrough curves of hexane isomers in MIL-140B at 343 K: a) 5 kPa, b) 10 kPa, c) 25 kPa, d) 37 kPa, and e) 50 kPa.

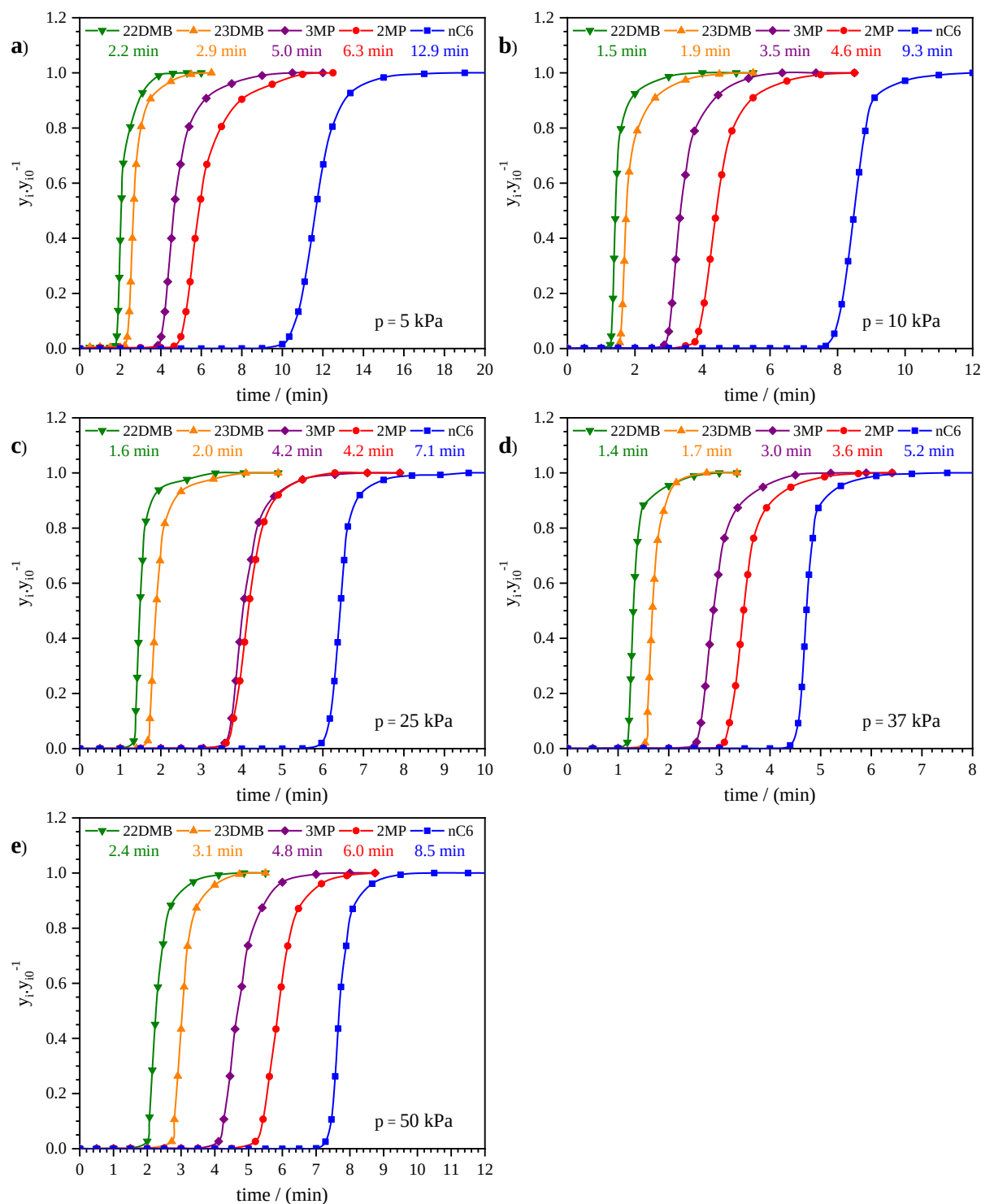


Figure C.2 | Experimental single component breakthrough curves of hexane isomers in MIL-140B at 373 K: a) 5 kPa, b) 10 kPa, c) 25 kPa, d) 37 kPa, and e) 50 kPa.

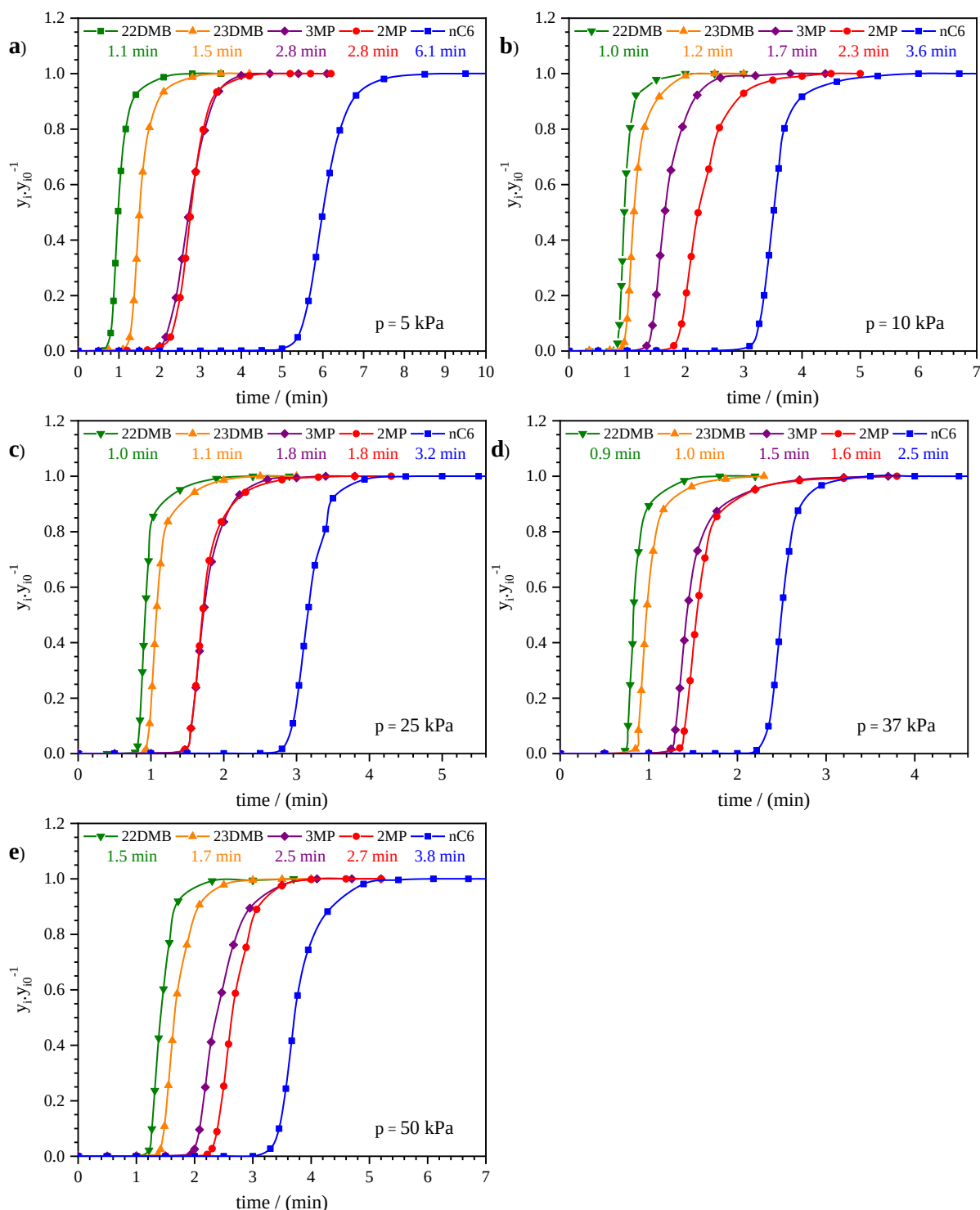


Figure C.3 | Experimental single component breakthrough curves of hexane isomers in MIL-140B at 423 K: a) 5 kPa, b) 10 kPa, c) 25 kPa, d) 37 kPa, and e) 50 kPa.

C.2 Multicomponent Adsorption of Hexane Isomers in MIL-140B

Tables C.1, C.2, and C.3 summarise the model parameters used in the numerical simulations of the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at the temperatures of 343, 373, and 423 K, respectively.

Table C.1 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 343 K.

T	(K)	3.43×10^2	3.43×10^2	3.43×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	3.51×10^1	3.51×10^1	3.51×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.48×10^1	5.59×10^1	9.10×10^1
D_{ax}	(m ² .s ⁻¹)	3.22×10^{-5}	2.62×10^{-5}	2.30×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	1.87×10^{-5}	1.01×10^{-5}	5.52×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	1.43×10^{-5}	8.24×10^{-6}	4.66×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.33×10^{-5}	7.76×10^{-6}	4.42×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	1.64×10^{-5}	9.05×10^{-6}	5.00×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	1.53×10^{-5}	8.71×10^{-6}	4.89×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	8.96×10^1	5.90×10^1	4.04×10^1
h_w	(W.m ⁻² .K ⁻¹)	5.99×10^{-2}	9.61×10^{-2}	1.56×10^{-1}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.41×10^{-1}	3.21×10^{-1}	4.58×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	8.81×10^{-2}	4.87×10^{-2}	2.59×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.34×10^{-5}	9.35×10^{-6}	7.05×10^{-6}
v_{int}	(m.s ⁻¹)	1.53×10^{-2}	1.53×10^{-2}	1.53×10^{-2}
a_c	(m ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
a_p	(m ⁻¹)	2.40×10^3	2.40×10^3	2.40×10^3
ρ_b	(kg.m ⁻³)	5.17×10^2	5.17×10^2	5.17×10^2
d_p	(m)	2.50×10^{-3}	2.50×10^{-3}	2.50×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2	9.00×10^2
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table C.2 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 373 K.

T	(K)	3.73×10^2	3.73×10^2	3.73×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	3.22×10^1	3.22×10^1	3.22×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.60×10^1	5.88×10^1	9.69×10^1
D_{ax}	(m ² .s ⁻¹)	3.61×10^{-5}	2.92×10^{-5}	2.54×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	2.18×10^{-5}	1.19×10^{-5}	6.51×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	1.67×10^{-5}	9.66×10^{-6}	5.48×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.55×10^{-5}	9.09×10^{-6}	5.19×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	1.91×10^{-5}	1.06×10^{-5}	5.89×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	1.78×10^{-5}	1.02×10^{-5}	5.75×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	9.56×10^1	6.35×10^1	4.40×10^1
h_w	(W.m ⁻² .K ⁻¹)	6.19×10^{-2}	1.01×10^{-1}	1.67×10^{-1}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.52×10^{-1}	3.33×10^{-1}	4.78×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	9.46×10^{-2}	5.31×10^{-2}	2.88×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.43×10^{-5}	1.01×10^{-5}	7.64×10^{-6}
v_{int}	(m.s ⁻¹)	1.67×10^{-2}	1.67×10^{-2}	1.67×10^{-2}
a_c	(m ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
a_p	(m ⁻¹)	2.40×10^3	2.40×10^3	2.40×10^3
ρ_b	(kg.m ⁻³)	5.17×10^2	5.17×10^2	5.17×10^2
d_p	(m)	2.50×10^{-3}	2.50×10^{-3}	2.50×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2	9.00×10^2
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Table C.3 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-140B at 423 K.

T	(K)	4.23×10^2	4.23×10^2	4.23×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.84×10^1	2.84×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.79×10^1	6.35×10^1	1.06×10^2
D_{ax}	(m ² .s ⁻¹)	4.29×10^{-5}	3.42×10^{-5}	2.94×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	2.75×10^{-5}	1.51×10^{-5}	8.31×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	2.09×10^{-5}	1.22×10^{-5}	6.96×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.95×10^{-5}	1.15×10^{-5}	6.60×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	2.41×10^{-5}	1.35×10^{-5}	7.52×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	2.24×10^{-5}	1.29×10^{-5}	7.31×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	1.05×10^2	7.10×10^1	5.01×10^1
h_w	(W.m ⁻² .K ⁻¹)	6.51×10^{-2}	1.09×10^{-1}	1.83×10^{-1}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.68×10^{-1}	3.52×10^{-1}	5.09×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.05×10^{-1}	6.02×10^{-2}	3.36×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	1.58×10^{-5}	1.13×10^{-5}	8.59×10^{-6}
v_{int}	(m.s ⁻¹)	1.89×10^{-2}	1.89×10^{-2}	1.89×10^{-2}
a_c	(m ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
a_p	(m ⁻¹)	2.40×10^3	2.40×10^3	2.40×10^3
ρ_b	(kg.m ⁻³)	5.17×10^2	5.17×10^2	5.17×10^2
d_p	(m)	2.50×10^{-3}	2.50×10^{-3}	2.50×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2	9.00×10^2
ε_b	(-)	4.00×10^{-1}	4.00×10^{-1}	4.00×10^{-1}

Appendix D

D.1 Multicomponent Adsorption of Pentane and Hexane Isomers in MIL-160(Al) and Zeolite 5A

Figure D.1 illustrates the concentration profiles of the pentane and hexane isomers for each cycle of the PSA experiment performed in the mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A, at the temperature of 423 K and total alkane pressure of 50 kPa, until the CSS is reached. The corresponding pressure history at the column outlet is presented in Figure D.2. The data measured at 473 K are represented in Figures D.3 and D.4.

Tables D.1, D.2, and D.3 summarise the model parameters used in the numerical simulations of the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-160(Al), septenary equimolar mixture of pentane and hexane isomers in MIL-160(Al), and septenary equimolar mixture of pentane and hexane isomers in the mixed-bed of MIL-160(Al) and zeolite 5A, respectively.

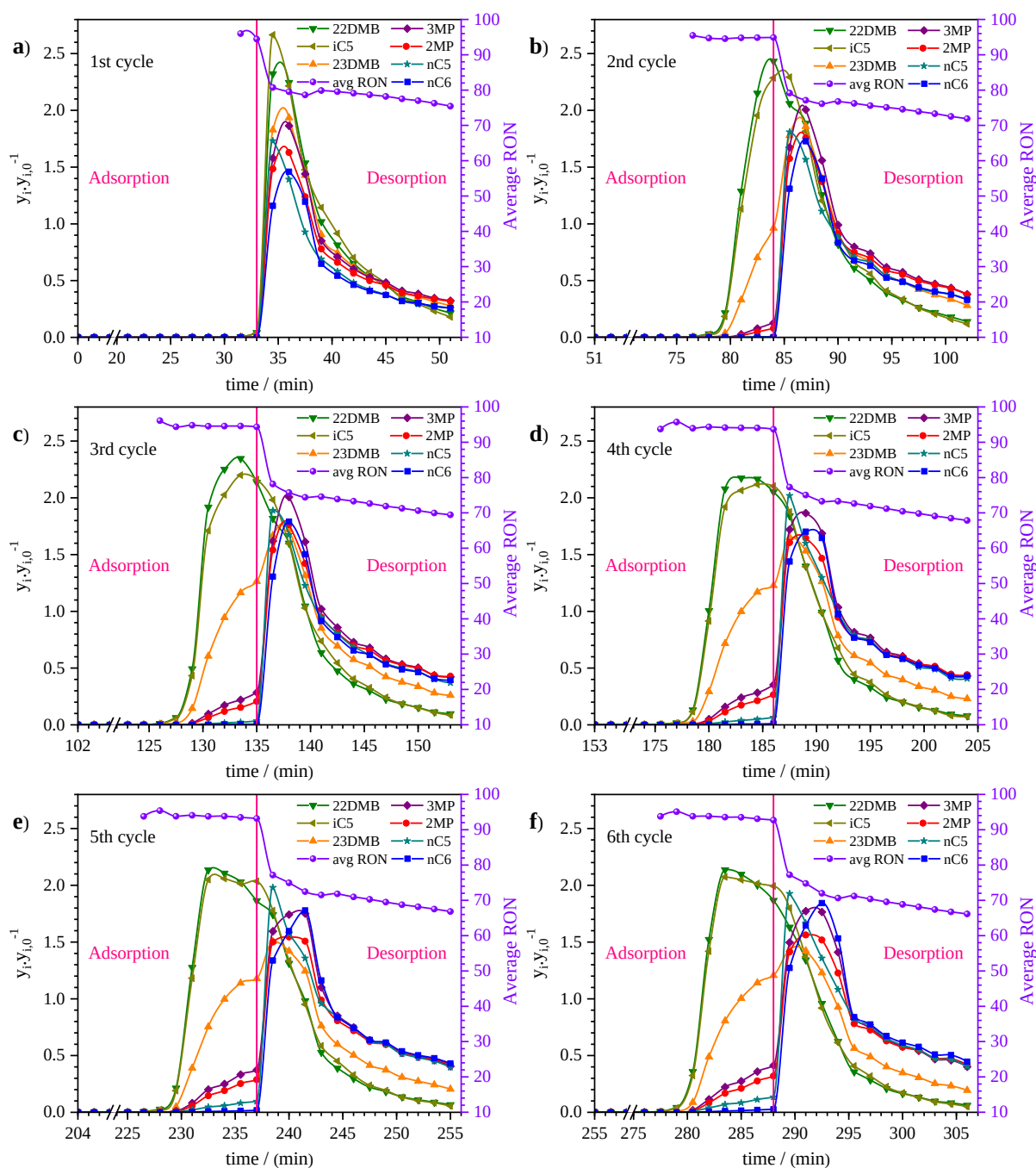


Figure D.1 | Evolution of the normalized molar fraction profiles of the pentane and hexane isomers along the continuous cyclic runs of a simplified PSA experiment in a mixed bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 423 K and 50 kPa: a) 1st cycle, b) 2nd cycle, c) 3rd cycle, d) 4th cycle, e) 5th cycle, and f) 6th cycle (CSS). Adsorption, step I - pressurization and feed; desorption, Step II – vacuum countercurrent depressurization followed by inert He purge.

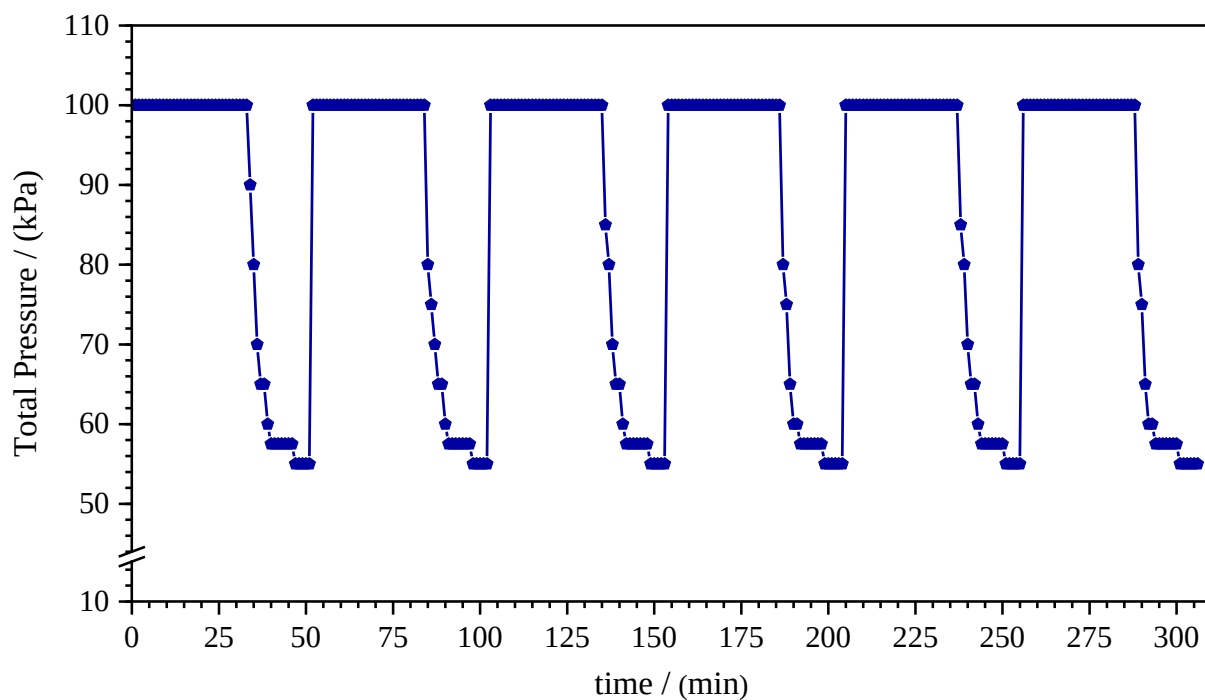
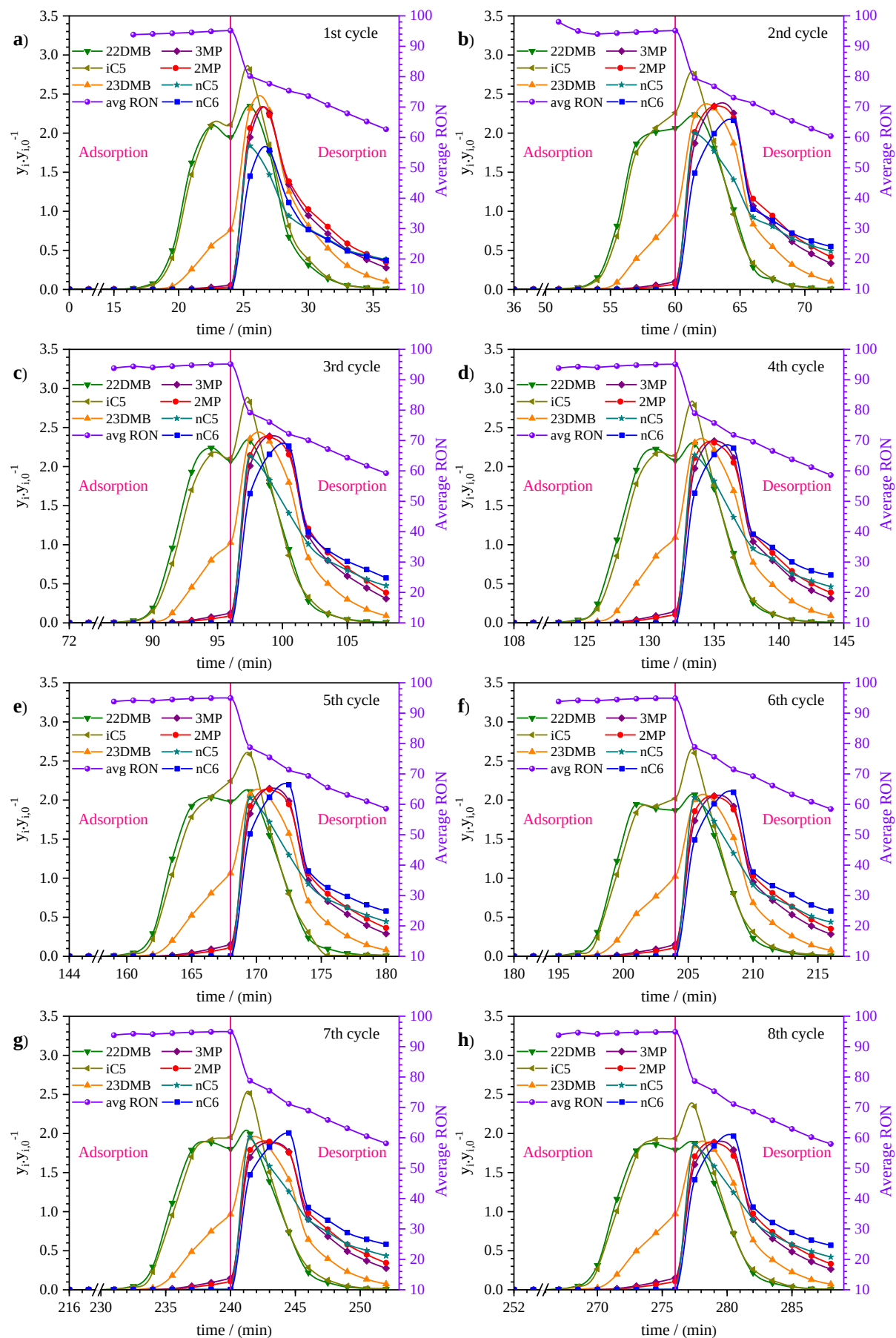


Figure D.2 | Pressure history at the column outlet during the continuous cyclic operation shown in Figure D.1.



(Continue on the next page)

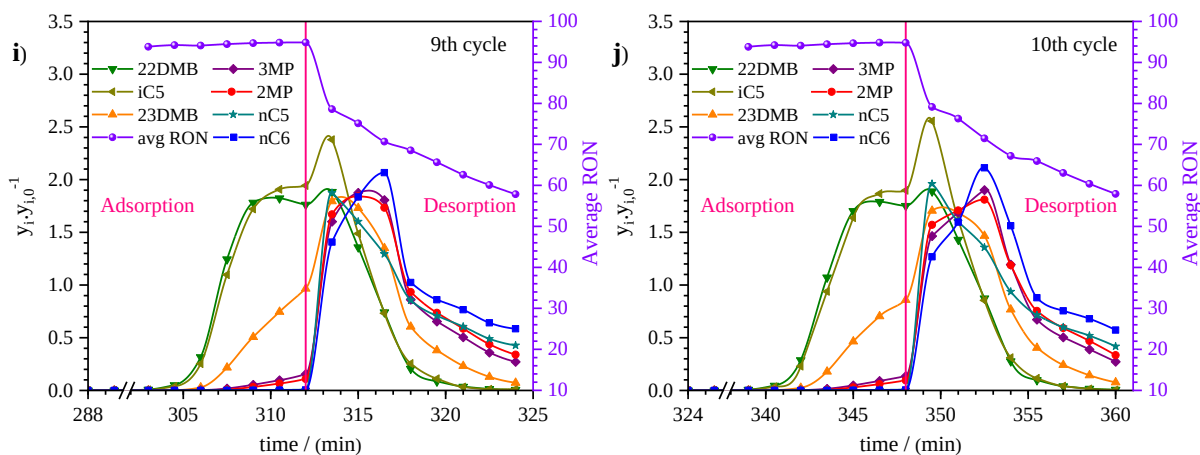


Figure D.3 | Evolution of the normalized molar fraction profiles of pentane and hexane isomers along the continuous cyclic runs of a simplified PSA experiment in a mixed bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 473 K and 50 kPa: a) 1st cycle, b) 2nd cycle, c) 3rd cycle, d) 4th cycle, e) 5th cycle, f) 6th, g) 7th cycle, h) 8th cycle, i) 9th cycle, and j) 10th cycle (CSS). Adsorption, step I - pressurization and feed; desorption, Step II – vacuum countercurrent depressurization followed by inert He purge.

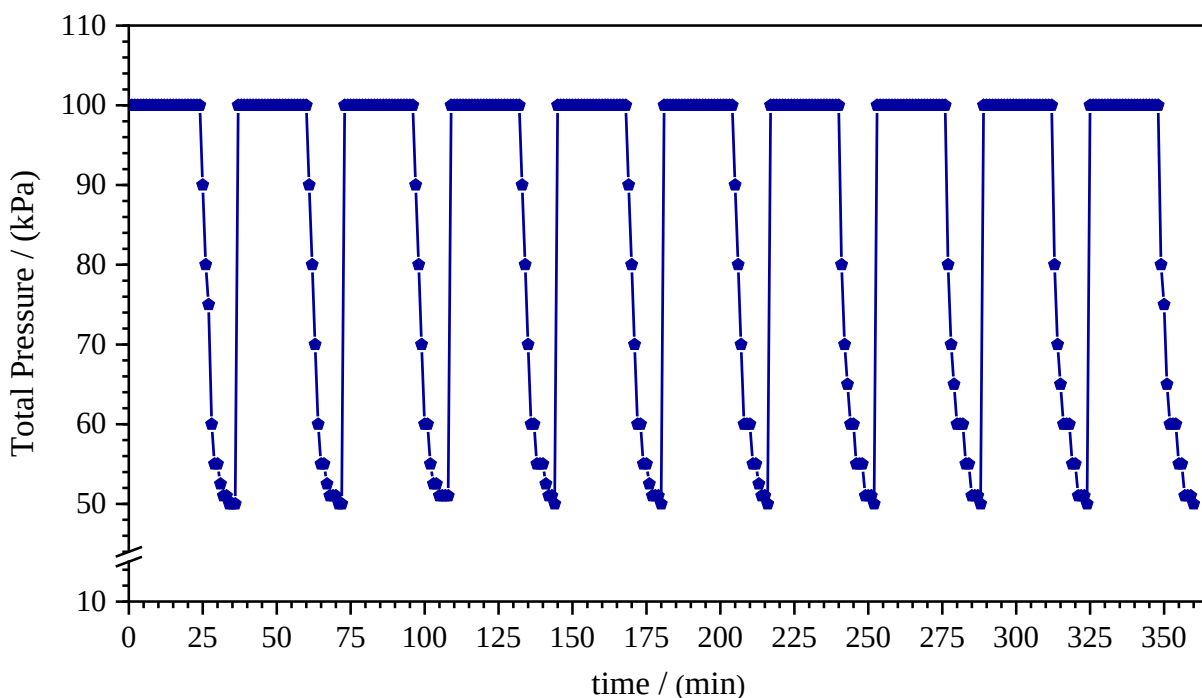


Figure D.4 | Pressure history at the column outlet during the continuous cyclic operation shown in Figure D.3.

Table D.1 | Model parameters for simulating the breakthrough curves for a quinary equimolar mixture of hexane isomers in MIL-160(Al) at 423 and 473 K.

T	(K)	4.23×10^2	4.73×10^2
p_T	(kPa)	5.00×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	1.06×10^2	1.15×10^2
D_{ax}	(m ² .s ⁻¹)	1.65×10^{-5}	1.79×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	8.31×10^{-6}	1.03×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	6.96×10^{-6}	8.59×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	6.60×10^{-6}	8.14×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	7.52×10^{-6}	9.32×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	7.31×10^{-6}	9.02×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	3.96×10^1	4.36×10^1
h_w	(W.m ⁻² .K ⁻¹)	2.83×10^0	2.74×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	2.53×10^{-1}	2.54×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	3.36×10^{-2}	3.84×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	8.59×10^{-6}	9.50×10^{-6}
v_{int}	(m.s ⁻¹)	8.00×10^{-3}	8.00×10^{-3}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	2.25×10^3	2.25×10^3
ρ_b	(kg.m ⁻³)	5.01×10^2	5.01×10^2
d_p	(m)	2.70×10^{-3}	2.70×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2
ε_b	(-)	4.45×10^{-1}	4.45×10^{-1}

Table D.2 | Model parameters for simulating the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in MIL-160(Al) at 423 and 473 K.

T	(K)	4.23×10^2	4.73×10^2
p_T	(kPa)	5.00×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	1.02×10^2	1.10×10^2
D_{ax}	(m ² .s ⁻¹)	2.58×10^{-5}	2.63×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	9.60×10^{-6}	1.19×10^{-5}
D_{miC5}	(m ² .s ⁻¹)	9.65×10^{-6}	1.19×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	8.80×10^{-6}	1.09×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	7.21×10^{-6}	8.90×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	6.79×10^{-6}	8.38×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	7.87×10^{-6}	9.76×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	7.62×10^{-6}	9.40×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	4.84×10^1	5.22×10^1
h_w	(W.m ⁻² .K ⁻¹)	4.97×10^0	4.56×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.80×10^{-1}	3.51×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	3.66×10^{-2}	4.19×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}
μ_g	(Pa.s)	9.37×10^{-6}	1.04×10^{-5}
v_{int}	(m.s ⁻¹)	1.47×10^{-2}	1.40×10^{-2}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2
a_p	(m ⁻¹)	2.25×10^3	2.25×10^3
ρ_b	(kg.m ⁻³)	5.01×10^2	5.01×10^2
d_p	(m)	2.70×10^{-3}	2.70×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2
ε_b	(-)	4.45×10^{-1}	4.45×10^{-1}

Table D.3 | Model parameters for simulating the breakthrough curves for a septenary mixture of pentane and hexane isomers in a mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 423 and 473 K.

T	(K)	4.23×10^2	4.73×10^2
p_T	(kPa)	5.00×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	1.02×10^2	1.10×10^2
D_{ax}	(m ² .s ⁻¹)	2.31×10^{-5}	2.44×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	9.60×10^{-6}	1.19×10^{-5}
D_{miC5}	(m ² .s ⁻¹)	9.65×10^{-6}	1.19×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	8.80×10^{-6}	1.09×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	7.21×10^{-6}	8.90×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	6.79×10^{-6}	8.38×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	7.87×10^{-6}	9.76×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	7.62×10^{-6}	9.40×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	5.27×10^1	5.83×10^1
h_w	(W.m ⁻² .K ⁻¹)	4.78×10^0	4.63×10^0
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.74×10^{-1}	3.62×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	3.66×10^{-2}	4.19×10^{-2}
k_{s_MOF}	(W.m ⁻¹ .K ⁻¹)	1.73×10^{-1}	1.73×10^{-1}
$k_{s\_zeolite}^1$	(W.m ⁻¹ .K ⁻¹)	2.63×10^{-1}	2.63×10^{-1}
k_{s_avg}	(W.m ⁻¹ .K ⁻¹)	2.00×10^{-1}	2.00×10^{-1}
μ_g	(Pa.s)	9.37×10^{-6}	1.04×10^{-5}
v_{int}	(m.s ⁻¹)	1.44×10^{-2}	1.44×10^{-2}
a_c	(m ⁻¹)	4.00×10^2	4.00×10^2
a_{p_MOF}	(m ⁻¹)	2.25×10^3	2.25×10^3
$a_{p\_zeolite}$	(m ⁻¹)	3.75×10^3	3.75×10^3
a_{p_avg}	(m ⁻¹)	2.70×10^3	2.70×10^3
ρ_b	(kg.m ⁻³)	5.54×10^2	5.54×10^2
d_{p_MOF}	(m)	2.70×10^{-3}	2.70×10^{-3}
$d_{p\_zeolite}$	(m)	1.16×10^{-3}	1.16×10^{-3}
d_{p_avg}	(m)	2.23×10^{-3}	2.23×10^{-3}
c_{ps_MOF}	(J.kg ⁻¹ .K ⁻¹)	9.00×10^2	9.00×10^2
$c_{ps\_zeolite}^2$	(J.kg ⁻¹ .K ⁻¹)	9.20×10^2	9.20×10^2
c_{ps_avg}	(J.kg ⁻¹ .K ⁻¹)	9.06×10^2	9.06×10^2
ε_{b_avg}	(-)	4.36×10^{-1}	4.36×10^{-1}

D.2 References

- (1) Griesinger, A.; Spindler, K.; Hahne, E. Measurements and Theoretical Modelling of the Effective Thermal Conductivity of Zeolites. *Int. J. Heat Mass Transf.* **1999**, *42*, 4363–4374.
- (2) Liu, Z.; Grande, C. A.; Li, P.; Yu, J.; Rodrigues, A. E. Adsorption and Desorption of Carbon Dioxide and Nitrogen on Zeolite 5A. *Sep. Sci. Technol.* **2011**, *46*, 434–451.

Appendix E

E.1 Multicomponent Adsorption of Pentane and Hexane Isomers in 3D-Printed Monoliths

Figures E.1, E.2, and E.3 show the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in 3D-printed activated monoliths at the temperatures of 373, 423, and 473 K, respectively. In each figure, the effect of total alkane pressure is shown: a) 10 kPa, b) 25 kPa, and c) 50 kPa. Also, panel 1 (left) represents the data measured in monolith M2 while panel 2 (right) resemble to monolith M3. The corresponding septenary adsorption equilibrium isotherms obtained from these experiments are given in Figure E.4.

Tables E.1, E.2, and E.3 summarise the model parameters used in the numerical simulations of the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at the temperatures of 373, 423, and 473 K, respectively.

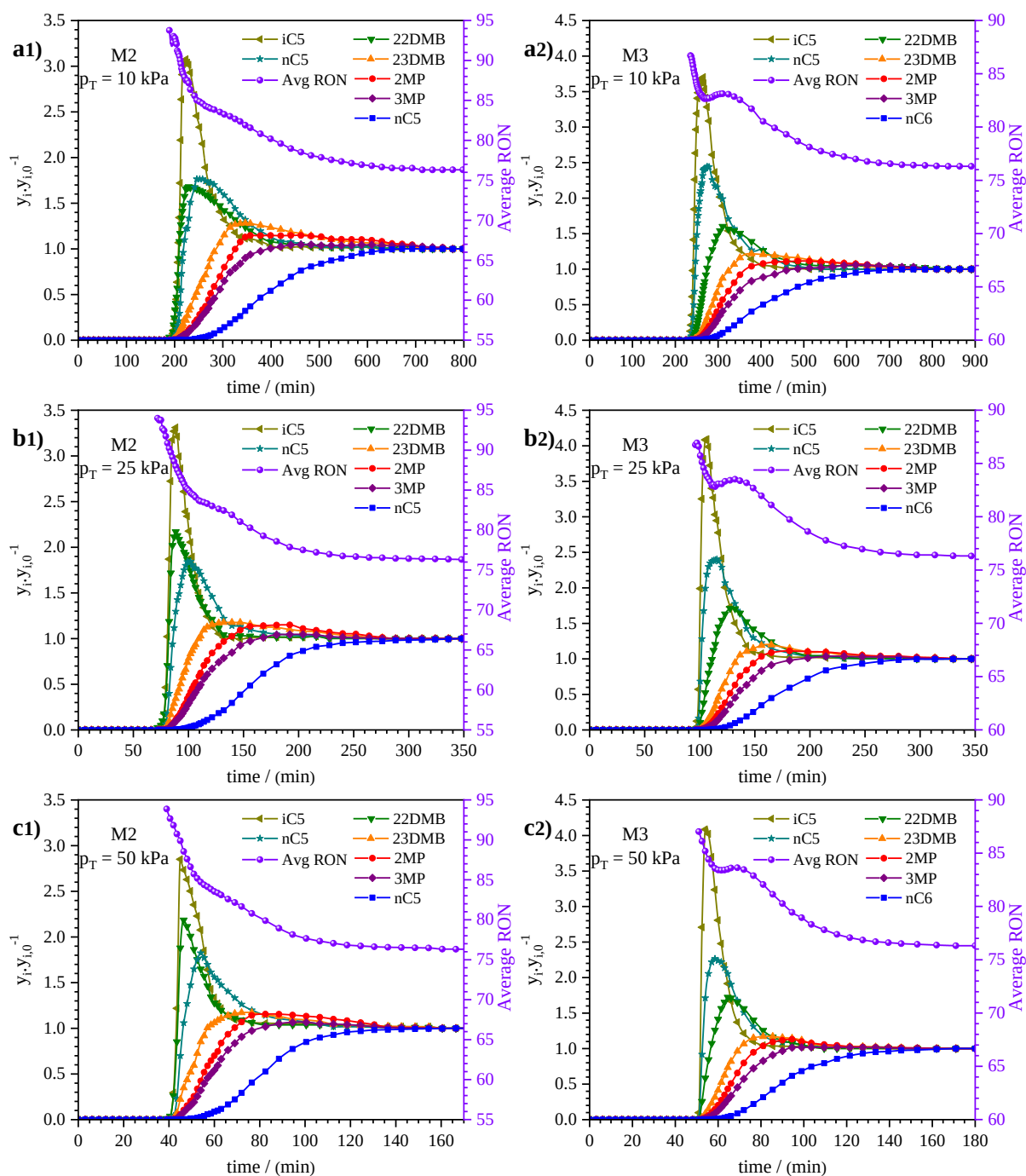


Figure E.1 | Experimental breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monoliths M2 (left, panel 1) and M3 (right, panel 2) at 373 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa.

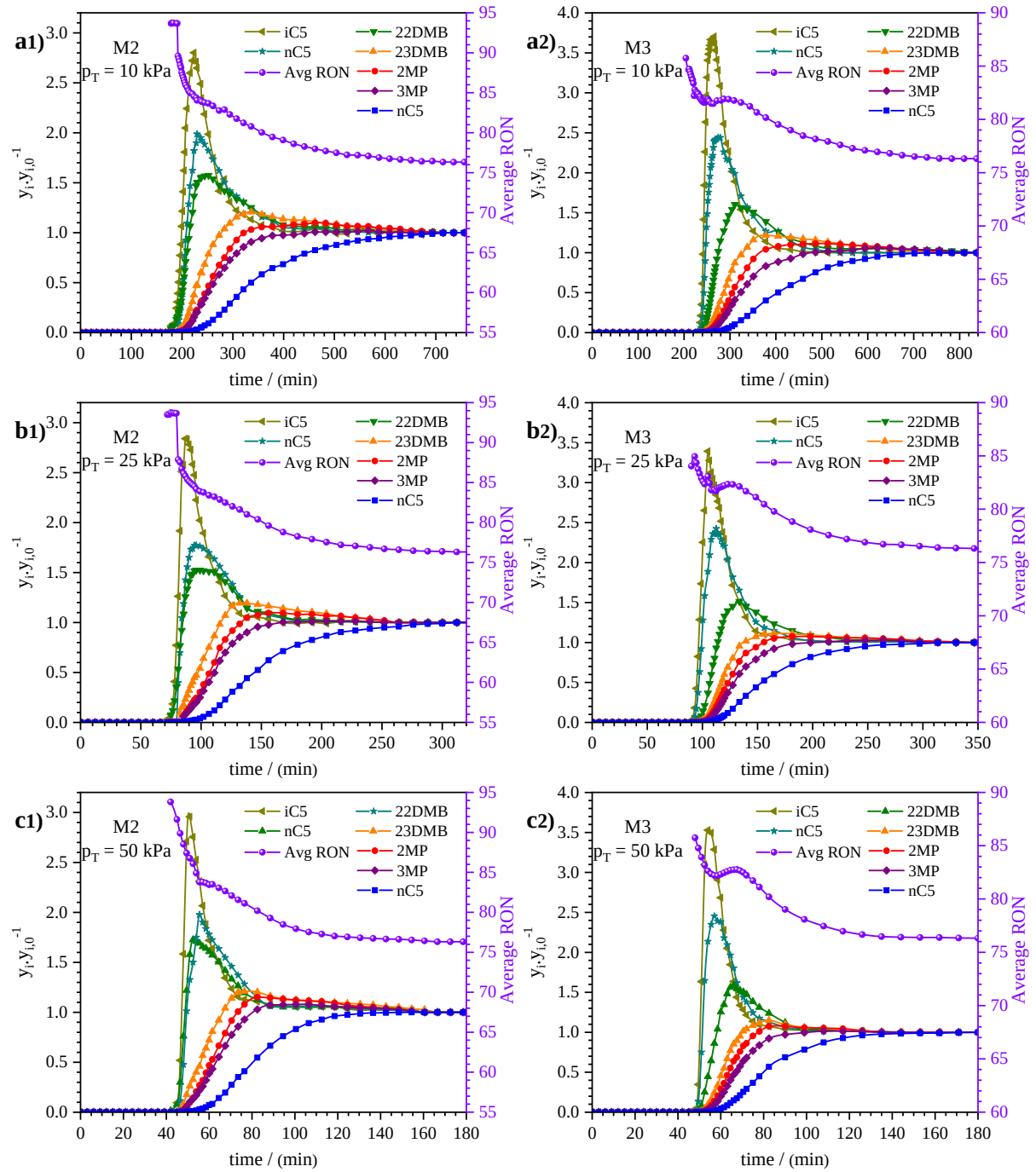


Figure E.2 | Experimental breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monoliths M2 (left, panel 1) and M3 (right, panel 2) at 423 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa.

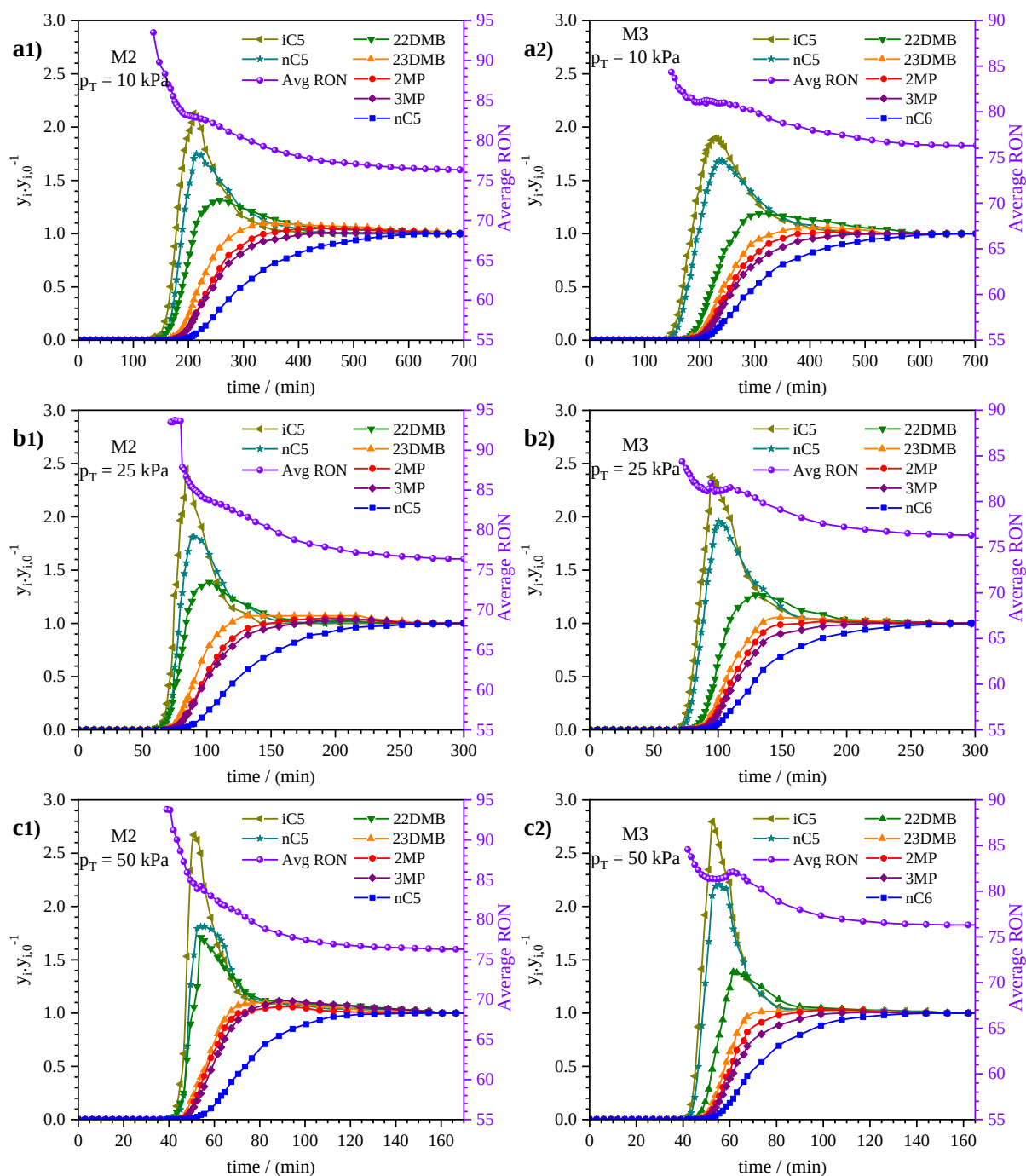


Figure E.3 | Experimental breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monoliths M2 (left, panel 1) and M3 (right, panel 2) at 473 K: a) 10 kPa, b) 25 kPa, and c) 50 kPa.

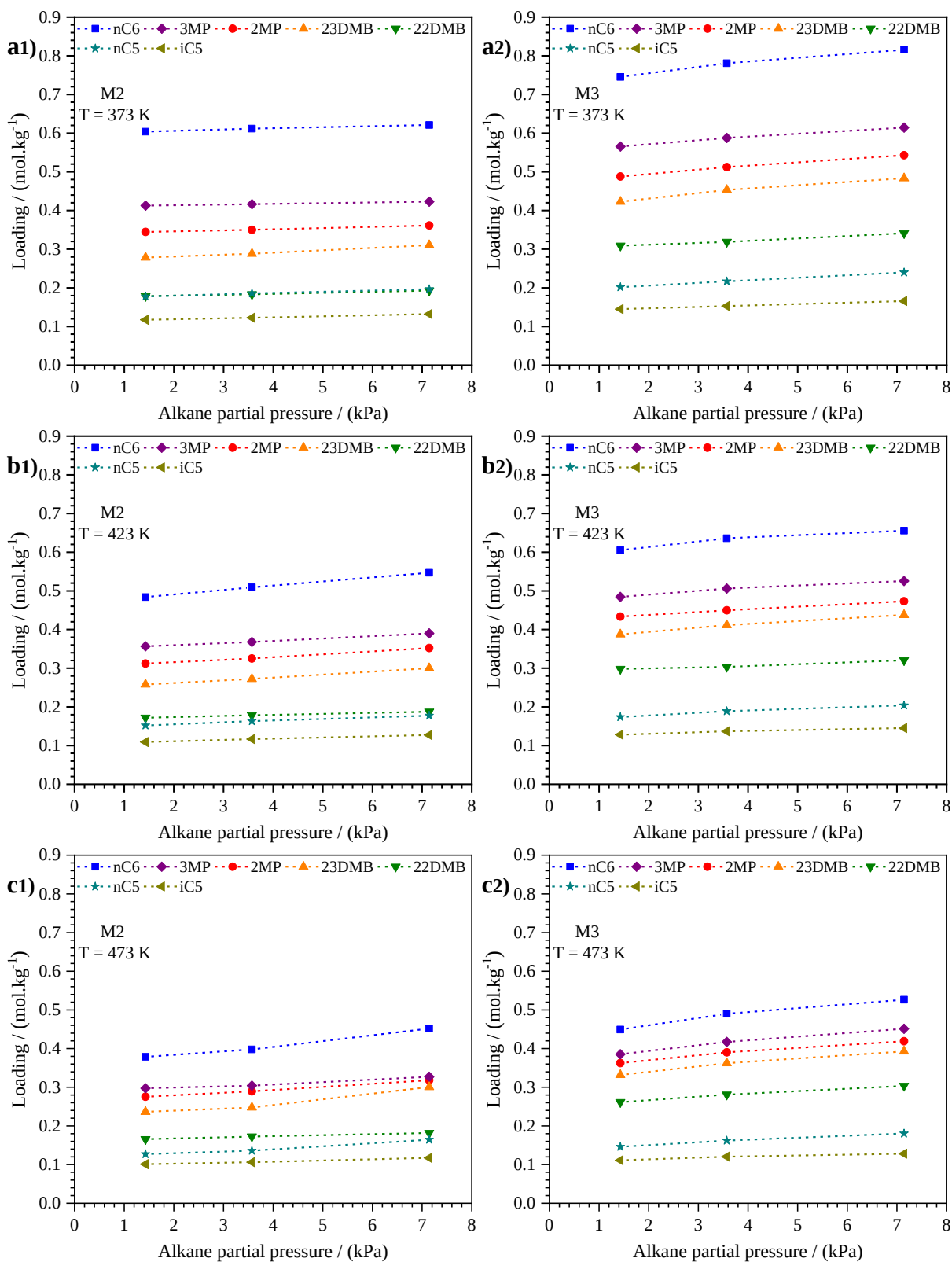


Figure E.4 | Septenary adsorption equilibrium isotherms of pentane and hexane isomers in monoliths M2 (left, panel 1) and M3 (right, panel 2): a) 373 K, b) 423 K, and c) 473 K.

Table E.1 | Model parameters for simulating the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 373 K.

T	(K)	3.73×10^2	3.73×10^2	3.73×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	3.22×10^1	3.22×10^1	3.22×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.52×10^1	5.68×10^1	9.28×10^1
D_{ax}	(m ² .s ⁻¹)	3.24×10^{-5}	2.54×10^{-5}	2.16×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	2.40×10^{-5}	1.34×10^{-5}	7.53×10^{-6}
D_{miC5}	(m ² .s ⁻¹)	2.41×10^{-5}	1.35×10^{-5}	7.57×10^{-6}
D_{mnC6}	(m ² .s ⁻¹)	2.23×10^{-5}	1.23×10^{-5}	6.89×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	1.68×10^{-5}	9.84×10^{-6}	5.67×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.56×10^{-5}	9.21×10^{-6}	5.35×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	1.94×10^{-5}	1.09×10^{-5}	6.17×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	1.80×10^{-5}	1.04×10^{-5}	5.99×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	3.11×10^1	2.09×10^1	1.45×10^1
h_w	(W.m ⁻² .K ⁻¹)	2.00×10^{-2}	3.23×10^{-2}	5.28×10^{-2}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.75×10^{-1}	2.88×10^{-1}	2.54×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	9.92×10^{-2}	5.70×10^{-2}	3.14×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	3.70×10^{-1}	3.70×10^{-1}	3.70×10^{-1}
μ_g	(Pa.s)	1.51×10^{-5}	1.09×10^{-5}	8.33×10^{-6}
v_{int}	(m.s ⁻¹)	4.20×10^{-3}	4.20×10^{-3}	4.20×10^{-3}
a_c	(m ⁻¹)	5.00×10^2	5.00×10^2	5.00×10^2
a_p	(m ⁻¹)	7.50×10^2	7.50×10^2	7.50×10^2
ρ_b	(kg.m ⁻³)	5.60×10^2	5.60×10^2	5.60×10^2
d_p	(m)	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
ε_b	(-)	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}

Table E.2 | Model parameters for simulating the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 423 K.

T	(K)	4.23×10^2	4.23×10^2	4.23×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.84×10^1	2.84×10^1	2.84×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.70×10^1	6.13×10^1	1.02×10^2
D_{ax}	(m ² .s ⁻¹)	3.65×10^{-5}	2.78×10^{-5}	2.30×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	3.02×10^{-5}	1.70×10^{-5}	9.60×10^{-6}
D_{miC5}	(m ² .s ⁻¹)	3.04×10^{-5}	1.71×10^{-5}	9.65×10^{-6}
D_{mnC6}	(m ² .s ⁻¹)	2.81×10^{-5}	1.57×10^{-5}	8.80×10^{-6}
D_{m2MP}	(m ² .s ⁻¹)	2.11×10^{-5}	1.24×10^{-5}	7.21×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	1.96×10^{-5}	1.17×10^{-5}	6.79×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	2.44×10^{-5}	1.39×10^{-5}	7.87×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	2.26×10^{-5}	1.32×10^{-5}	7.62×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	3.37×10^1	2.29×10^1	1.60×10^1
h_w	(W.m ⁻² .K ⁻¹)	1.85×10^{-2}	3.07×10^{-2}	5.10×10^{-2}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	3.97×10^{-1}	3.05×10^{-1}	2.63×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.10×10^{-1}	6.47×10^{-2}	3.66×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	3.70×10^{-1}	3.70×10^{-1}	3.70×10^{-1}
μ_g	(Pa.s)	1.67×10^{-5}	1.22×10^{-5}	9.37×10^{-6}
v_{int}	(m.s ⁻¹)	4.20×10^{-3}	4.20×10^{-3}	4.20×10^{-3}
a_c	(m ⁻¹)	5.00×10^2	5.00×10^2	5.00×10^2
a_p	(m ⁻¹)	7.50×10^2	7.50×10^2	7.50×10^2
ρ_b	(kg.m ⁻³)	5.60×10^2	5.60×10^2	5.60×10^2
d_p	(m)	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
ε_b	(-)	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}

Table E.3 | Model parameters for simulating the breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1 at 473 K.

T	(K)	4.73×10^2	4.73×10^2	4.73×10^2
p_T	(kPa)	1.00×10^1	2.50×10^1	5.00×10^1
C_t	(mol.m ⁻³)	2.54×10^1	2.54×10^1	2.54×10^1
c_{pg}	(J.mol ⁻¹ .K ⁻¹)	3.86×10^1	6.54×10^1	1.10×10^2
D_{ax}	(m ² .s ⁻¹)	4.09×10^{-5}	3.04×10^{-5}	2.44×10^{-5}
D_{mnC5}	(m ² .s ⁻¹)	3.70×10^{-5}	2.10×10^{-5}	1.19×10^{-5}
D_{miC5}	(m ² .s ⁻¹)	3.72×10^{-5}	2.11×10^{-5}	1.19×10^{-5}
D_{mnC6}	(m ² .s ⁻¹)	3.45×10^{-5}	1.94×10^{-5}	1.09×10^{-5}
D_{m2MP}	(m ² .s ⁻¹)	2.58×10^{-5}	1.53×10^{-5}	8.90×10^{-6}
D_{m3MP}	(m ² .s ⁻¹)	2.39×10^{-5}	1.43×10^{-5}	8.38×10^{-6}
D_{m23DMB}	(m ² .s ⁻¹)	3.00×10^{-5}	1.71×10^{-5}	9.76×10^{-6}
D_{m22DMB}	(m ² .s ⁻¹)	2.76×10^{-5}	1.62×10^{-5}	9.40×10^{-6}
h_f	(W.m ⁻² .K ⁻¹)	3.63×10^1	2.48×10^1	1.75×10^1
h_w	(W.m ⁻² .K ⁻¹)	1.73×10^{-2}	2.93×10^{-2}	4.93×10^{-2}
K_{ax}	(W.m ⁻¹ .K ⁻¹)	4.17×10^{-1}	3.22×10^{-1}	2.73×10^{-1}
k_g	(W.m ⁻¹ .K ⁻¹)	1.21×10^{-1}	7.23×10^{-2}	4.19×10^{-2}
k_s	(W.m ⁻¹ .K ⁻¹)	3.70×10^{-1}	3.70×10^{-1}	3.70×10^{-1}
μ_g	(Pa.s)	1.82×10^{-5}	1.34×10^{-5}	1.04×10^{-5}
v_{int}	(m.s ⁻¹)	4.20×10^{-3}	4.20×10^{-3}	4.20×10^{-3}
a_c	(m ⁻¹)	5.00×10^2	5.00×10^2	5.00×10^2
a_p	(m ⁻¹)	7.50×10^2	7.50×10^2	7.50×10^2
ρ_b	(kg.m ⁻³)	5.60×10^2	5.60×10^2	5.60×10^2
d_p	(m)	8.00×10^{-3}	8.00×10^{-3}	8.00×10^{-3}
c_{ps}	(J.kg ⁻¹ .K ⁻¹)	1.00×10^3	1.00×10^3	1.00×10^3
ε_b	(-)	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}

